Master's Thesis

Upconverting Nanocrystal Based Microstructure Array Fabrication

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Abstract

Microstructure refers to the small scale structures of materials that can be revealed under magnification higher than 25X. Since microstructure of a material improve physical properties that determines application of a materials such as toughness, ductility, hardness, there have been many attempts to use micro-sized structures in various fields such as electrochemical device and sensors. Especially, these attempts are achieved by fabricating microstructure in array form. By arraying large numbers of microstructure on a single device, it can improve performance by reducing cost and volume. Thanks to these advantages, microstructure array represent an economic research tool, which has been greatly developed in not only various analysis, but also electrochemical devices. Because these microstructure devices are key components in a wide range of products such as electrochemical devices or analysis tool, microstructure array fabrication technique has become the core technology of the manufacture. In this study, we demonstrate some approaches to show various microstructure array fabrication techniques. In order to realize these fabrication technique, various optical instruments were manufactured ranging from DMD based microlithography technique to contact lithography. To demonstrate effectiveness of these microfabrication techniques, various photocurable resins were tested. First, we used conventional photocurable resins to show fabrication techniques. To find the optimal photocurable resin, resins with various property were used. We will cover several properties of these photocurable resins and utility of each method in this paper. To overcome physical properties of conventional photocurable resins, newly designed photocurable resins such as polyurethane-based resin, Polydimethylsiloxane-based resin, were synthesized and its property and utility was tested. These resins were used in microfabrication technique practically. Since the newly synthesized photocurable resin has excellent properties, it is expected to be applied not only to this process but also to various fields. To show applicability of this microstructure fabrication techniques, we present a new type of microstructure array which consists of Upconverting Nanocrystals (UCNs). UCNs are lanthanide doped inorganic nano-size crystal, which can be excited with near infrared (NIR) light and emit anti-stokes fluorescence in visible spectrum. By regulating lanthanide dopant concentration, it can emit various color of visible light. We synthesized hexagonal-phase UCNs in rod shape by hydrothermal method, and observed its optical property. To fabricate UCNs-integrated microstructure array perfectly, we discuss surface modification and dispersion process of UCNs with various photocurable resin. The methods described here are an easy way to modify UCNs surface for dispersion with photocurable resin and let nanoparticle will be more used in polymer applications. By adopting UCNs, it is possible to create a new concept of microstructure array that respond to near-infrared rays.

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1. Introduction: Research Background for the Upconverting Nanocrystal based Microstructure array Fabrication

1.1 Microstructure array fabrication techniques

In recent years, as optics and micro-technology has been developed, new requirements have brought opportunities to functional microstructure which refers to the small scale structures that can be observed under magnification higher than 25X[1]. Since microstructure of a material improve physical properties that determines application of a materials such as toughness, ductility, hardness, there have been many attempts to use micro-sized structures in various fields such as electrochemical device and sensors. Especially, these attempts are achieved by fabricating microstructure in array form. By arraying large numbers of microstructure on a single device, it can improve performance by reducing cost and volume. Thanks to these advantages, Microstructure array represents an economic research tool, which can be applicable as biosensors, chemical sensors and be integrated into different electrochemical devices such as on-chip supercapacitors, microbatteries[2-6] (**Figure 1**). Because these microstructure devices are key components in a wide range of products, microstructure array fabrication technology is essential to modern science and technology and it has become the core technology of the manufacture. It is useful to fabricate a microstructure with both a high durability and a complex shape. There are many methods for the fabrication of microstructure. The major concepts and principles of microfabrication can be divided into various method such as photolithography, microforming, etching and soft lithography by how to transfer the pattern to the desired substrate[7-9]. Each method can be also divided into various way (**Figure 2**). For example, soft lithography include replica molding, micromolding in capillaries, micro-contact printing and micro-transfer molding[10-14]. This method is low cost and applicable to almost all polymers unlike photolithography. It can be used in various research, but there are definite defects. Because soft materials are used, mold or stamp can deformed and it makes this technique difficult to be used manufacturing process[15-17]. Because of these reason, microfabrication technology is usually constructed using photolithography. Photolithography uses light especially UV region, to transfer a designed pattern from photomask using a photocurable resin on the substrate. It can be classified in many ways by the way the photocurable resin is placed on the substrate, the way the light is transmitted, and so on. For example, whether photomask is used or not, they can be divided into maskless lithography which makes pattern by modulating light pattern using device such as digital micromirror device (DMD) [18-19]. In this article, we will demonstrates various method of lithographic technique and determine the microstructure array based on photolithography. In order to realize these fabrication method, we used many optical instrument such as optical microscope, UV-LED and furthermore

made several optical device directly. Since we are discussing UV-based photolithoraphy, we need to talk about the photopolymer that reacts to light in ultraviolet region. In normal photolithography procedure, monomer is mixed with photoinitiator which is compound that decompose into reactive species that activate polymerization of monomers upon radiation of light. After mixing monomer of photopolymer with photoinitiators, mixture was exposed to UV light. That results in hardening of polymeric material which is called as a crosslinking. In this way, commercial photocurable resins were tested and used to prove utility of our systems in photolithography technique. First, we used conventional photocurable resins to show fabrication techniques. To explore different monomer chemistries, we prepared conventional photocurable resins such as hydrophobic poly(urethane) acrylate (PUA), hydrophilic poly(ethylene glycol) diacrylate (PEGDA), 1,6-Hexanediol diacrylate (HDDA). To find the optimal photocurable resin, various property of each resin should have been considered. We will cover the physical and optical properties of these photocurable resins and utility of each method in this paper. Next, In order to complement the deficient properties of the commercial product, we synthesized the photocurable resin by ourselves. Newly designed photocurable resin such as Polyurethane-based resin, Polydimethylsiloxane-based resin was synthesized and their property and utility was tested in micro-fabrication. Since the newly synthesized photocurable resin has excellent properties including excellent elongation and flexibility, they are expected to be applied not only to this microfabrication process but also to various fields.

1.2 Upconverting Nanocrystals (UCNs)

Furthermore, we applied Upconverting nanocrystals (UCNs) to a microstructure array. Upconversion is an optical process that convert lower-energy photons into higher-energy photons and can be observed mainly in the rare earth elements such as lanthanide series[20-22]. UCNs are lanthanide doped inorganic nano-size crystal, which can be excited with near infrared (NIR) light and emit anti-Stokes fluorescence in visible spectrum range[23-24]. UCNs has excellent characteristics as optical material. It can express various colors at a single wavelength through concentration change of dopant. It has no background auto-fluorescence and is optically stable. It is also less toxic than other luminescent material, making it easy to be handled. It is known that UCNs can be present in various crystal phase such as cubic phase and hexagonal phase, and luminescent efficiency is the highest when it is synthesized as hexagonal phase. In this work, hexagonal phase rod shaped crystal doped with upconverting lanthanide ions (Er^{3+}, Yb^{3+},Tm^{3+}) was synthesized by hydrothermal method which is very simple and its synthetic yield is very high compared to other methods

such as thermal decomposition reaction. $NaYF_4$ was chosen as the host material because it is known as one of the best host materials for upconverting lanthanide ions. When doping Yb^{3+}, Er^{3+} and Tm^{3+} ions into $NaYF_4$ nanocrystal and Gd^{3+} is codoped for phase control of crystal, the efficiency of upconversion luminescence is much higher than luminescence for other nanocrystal[25-27]. During the synthesis, hydrophobic oleic acid was used as a capping agent which covers the surface of nanocrystal and prevent them from aggregation. Because crystal surface was capped by hydrophobic oleic acid, it results in hydrophobicity of UCNs. Hydrophobicity of crystal disturb dispersion quality of UCNs with various kinds of resin. To overcome this, several surface modification methods such as surface oxidation and silica coating, have been developed. Using these kind of method, surface chemistry of UCNs can be changed depending on the solution to be dispersed. Because it has various advantages like above, it can be used for various purposes ranging from biosensing to drug delivery and therapy[28-34]**(Figure 3).** To take advantage of UCN's these properties, we presents a new type of microstructure array which consists of Upconverting Nanocrystals (UCNs). To integrate UCNs into polymers, we also discussed the dispersion of nanoparticles in polymers. By adopting UCNs, it is possible to create a new concept of microstructure array that respond to near-infrared rays. By using not a just photocurable solution but a UCN dispersed photocurable resin, we can fabricate UCNs contained microstructure.

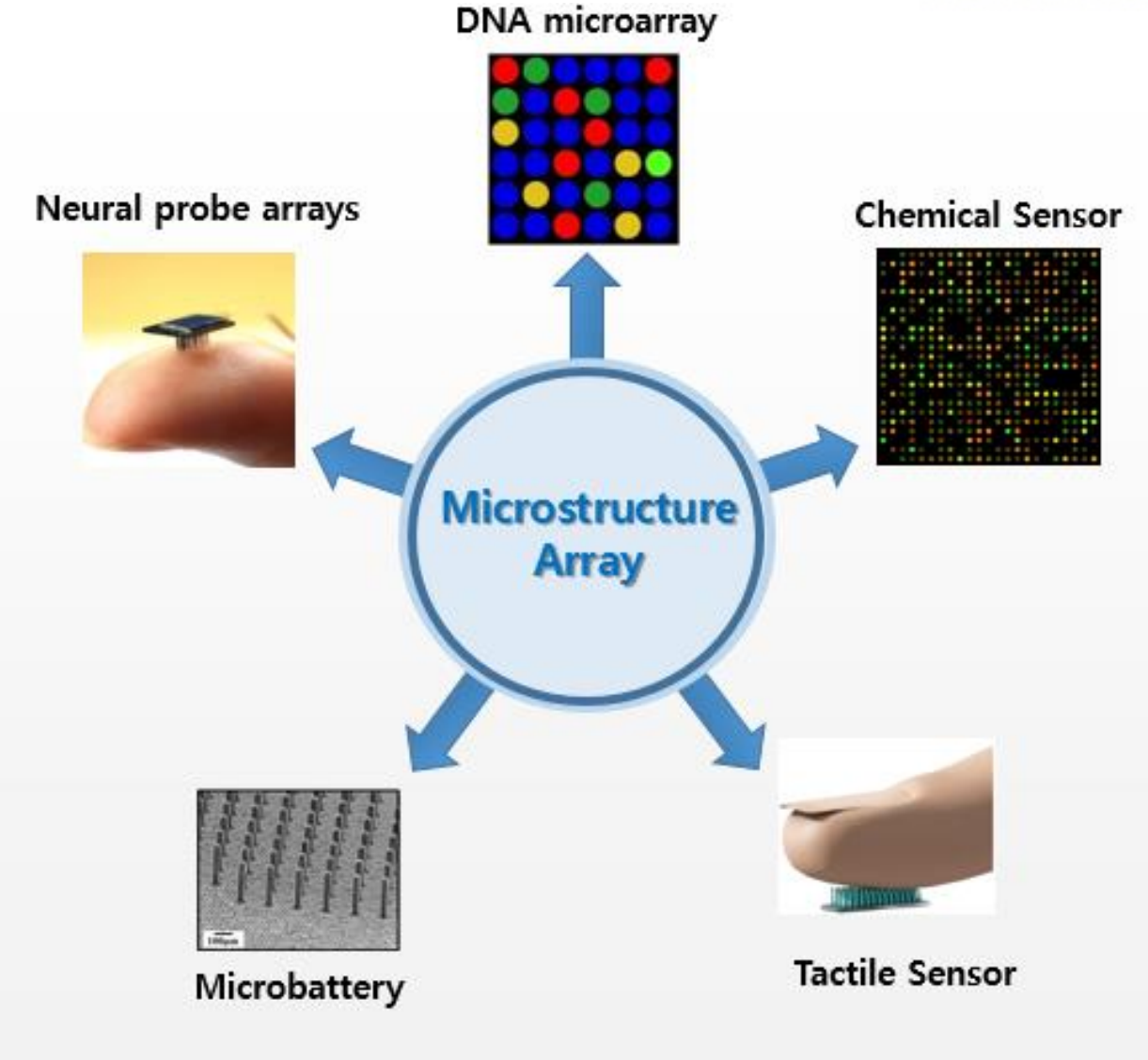


Figure 1. Overview of applications of microstructure array in different sectors ranging from DNA microarray to tactile sensor, chemical sensor, micro-batteries and neural probe arrays.

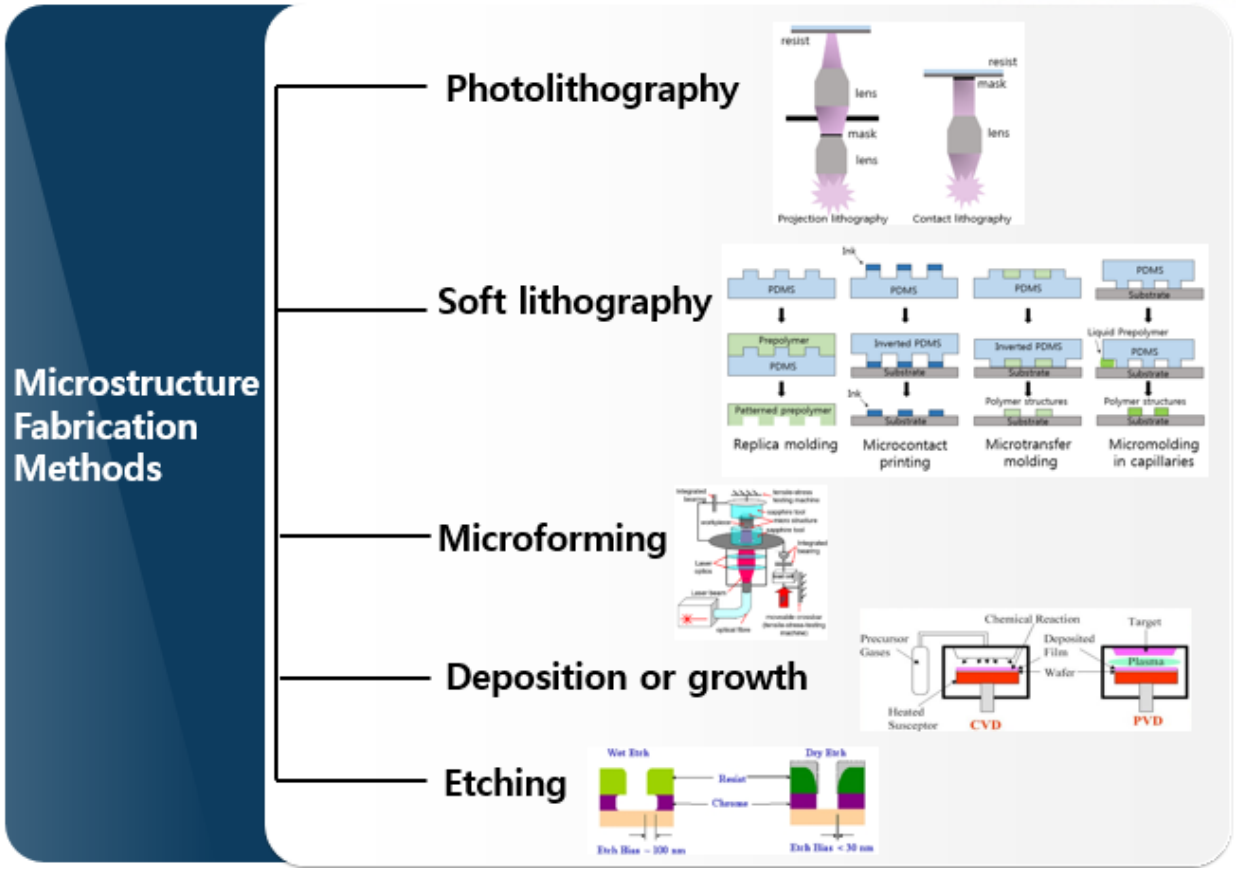


Figure 2. Various kinds of microstructure fabrication methods classified by how to transfer the pattern to substrate.

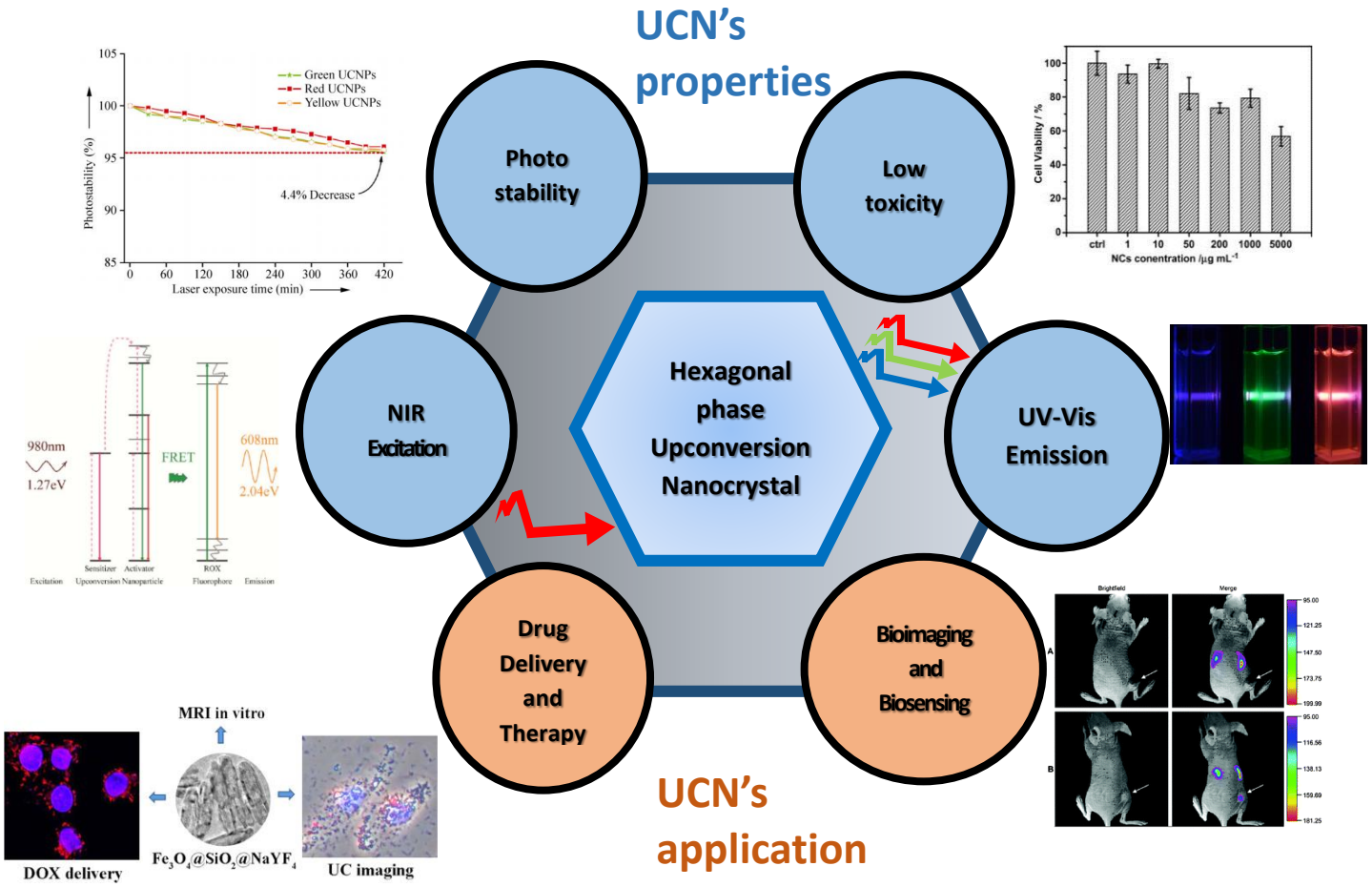


Figure 3. Overview of UCN's properties and applications of UCNs in different sectors ranging from Bioimaging to therapy and bioassays.

2. Microstructure array fabrication

Since the need for microstructure arrays has been around for a long time, various fabrication methods for microstructure array have been developed. Here we describe the fabrication of microstructure array in various method ranging from molding to DMD based maskless lithography and contact lithography. We made UV-based microstructure array fabrication platform based on Contact lithography and DMD based fabrication platform was also constructed by mounting it on a microscope **(Figure 4).** Each method has own advantages and disadvantages, and can be used selectively for specific purpose. Several microstructure arrays were fabricated to verify each method. In order to assure the functionality of these microstructures and fabrication techniques, the relationships between the microstructure designs and the manufacturing process have to be understood.

2.1 Microstructure array fabrication using molding technique

Molding is the process of manufacturing by shaping raw material using a rigid frame called a mold. It can generate micro-patterns and forms microstructures in materials by using micro-patterned mold. Silicon wafer is normally used as a mold because it has many advantages. Silicon is very abundant element, so that is very cheap to be used in manufacture, and it is atomically flat[35]. In addition, silicon has good current characteristics and relatively high melting point and operating temperature. After silicon wafer processing based on conventional photolithography, silicon wafer can become micro-patterned[36]. As one master wafer can be used to fabricate a large number of microstructures using a Prepolymer which is cross-linked. We chose conventional polydimethylsiloxane (PDMS) Sylgard184 as soft material in microstructure array manufacture process. The PDMS base and the curing agent are mixed at a ratio of 10: 1, and then PDMS is filled with a mold. After equilibrating, it is heated at 65°C for 3 hours. Dome shaped structure with a diameter of 100um was made (**Figure 5(a)**). Depending on how the mold is made, the structures can be made in various size. Dome shaped structure with a diameter of 45um was made (**Figure 5(b)**). This kind of micro-fabrication can be prepared by replica molding. A replica mold can be cast from the object to be replicated. This mold is then filled with a prepolymer, which is cross-linked. After curing, polymer is peeled from the mold. Because replica mold copy the shape of a silicon master wafer[37-38], multiple copies of original object can be manufactured without damaging the original mold. Based on microstructure in Figure 4(b), replica mold was manufactured using PDMS (**Figure 5(c)**). Replica molding with a PDMS mold can provide equally patterned microstructure with original object. Molding is a procedure that accommodates a wider range of materials than does photolithography. Unlike photolithography, where only photocurable

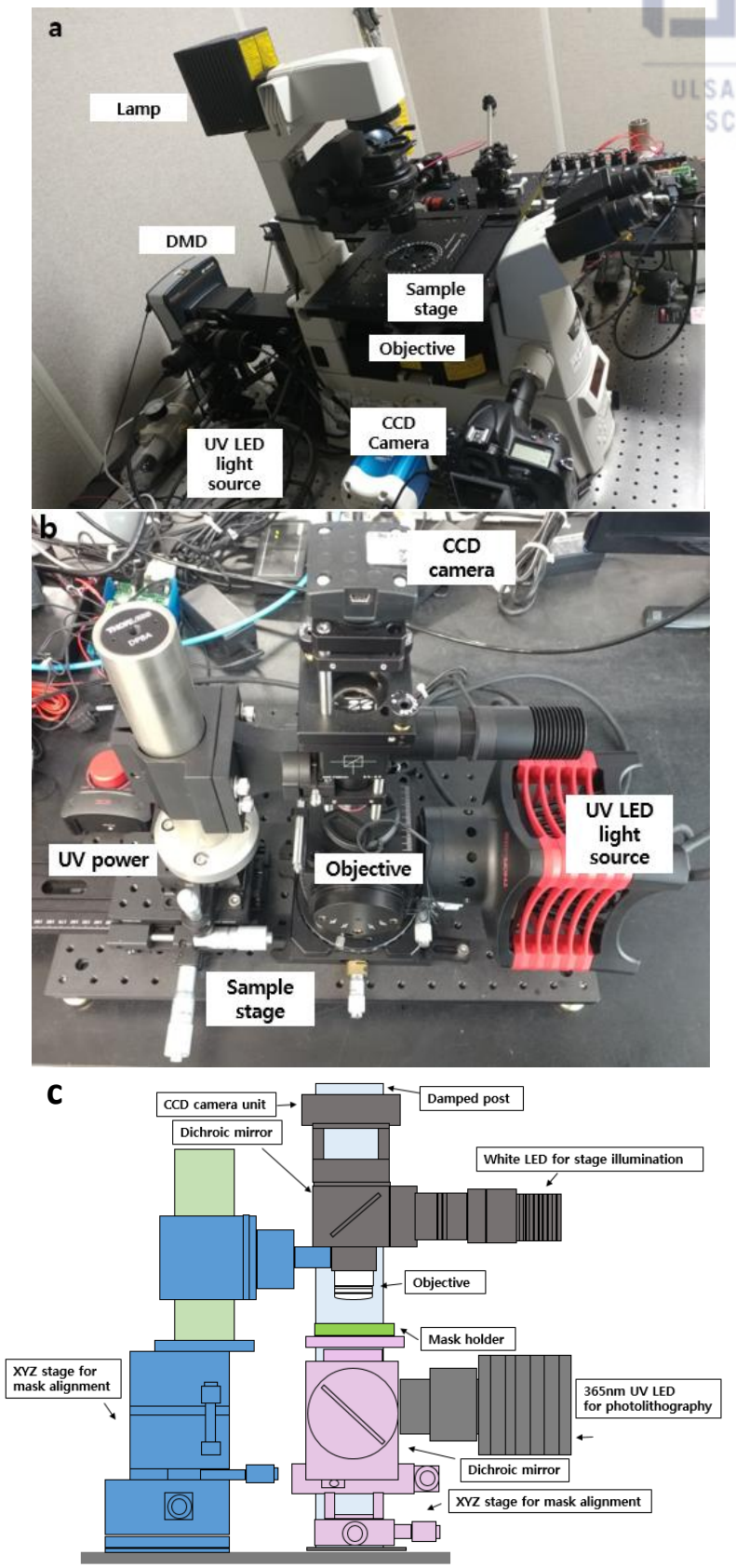


Figure 4. Microstructure fabrication methods. (a) DMD based lithography platform which is used by being mounted on a microscope, (b) Contact lithography platform (c) Schematic diagram of Contact lithography platform

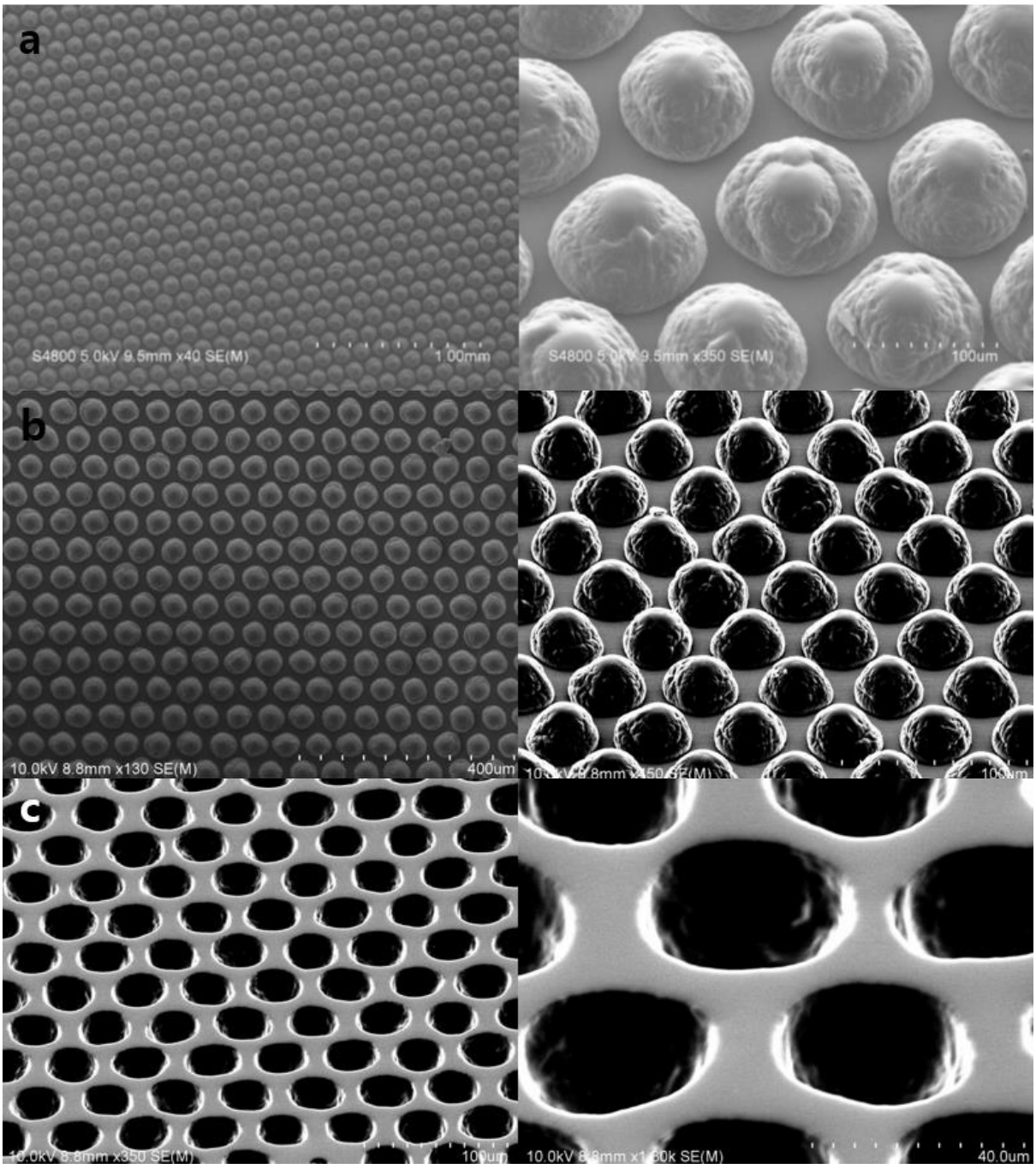


Figure 5. SEM image of Microdome array fabricated by molding technique. Microdome structure array with a diameter of (a) 100um, (b) 45um was made of PDMS. (c) Replica mold with a diameter of 45um was made of PDMS

solution is used, various materials such as thermosetting materials can be used in this kind of molding technique. It can be also used in duplication of three-dimensional structures in a single step, whereas conventional photolithography is not able to replicate such structures. The disadvantage of the molding technique is that the mold should be manufactured with the conventional lithography technique when new pattern is needed. This additional steps cause a time cost and an economical cost when performing double patterning lithography. The feature of the molding technique is also that the microstructure and the substrate are made of the same material. This can serve as a disadvantage because it can't be used for certain applications when specific substance is only added to a microstructure not a substrate. For that purpose, a method to cure the microstructure on the substrate, is needed.

2.2. Microstructure array fabrication using Digital micromirror device (DMD)

As the most successful and main manufacturing technology in micro-fabrication, photolithography plays a great role. In conventional photolithography, a photomask is used to pattern light, and the patterned light cures the photocurable resin. To fabricate various structure, corresponding patterned photomasks are required incurring the cost of generating a new photomask. To solve this problem, maskless lithography cab be used. Maskless lithography projects a precise light directly onto the photocurable resin without using a mask. In maskless lithography, the radiation used to expose a photocurable resin, is not transmitted through, a photomask[39]. Instead, by focusing on a narrow beam, radiation writes the image directly to the photoresist with one or more pixels at a time. The main advantage of maskless lithography is that the lithographic pattern can be changed from one run to the next run without the cost of creating a new photomask, which is useful for various patterning at the same time. To realize maskless lithography, we adopted concept of Digital micromirror device (DMD) which has become one of the most important devices in projection display field. DMD chips are adopted as the dynamic or virtual masks generator with the help of aluminum micro-mirrors and it projects the virtual masks to photocurable resin. On the surface of DMD chip, there are hundred thousand of microscopic mirrors arranged in a rectangular array corresponding to pixels in the image to be displayed. The mirrors can be individually rotated to turn them on or off. When turned on, the light from the projector bulb is reflected by the lens, and the pixels appear bright on the screen. In the off state, the light is sent to another place, so the pixels look dark[40-41]. Because DMD can be treat as a kind of spatial light modulator, we can fabricate various shape of microstructure by regulating DMD figure. The microstructure array fabrication is done on a specially designed stage **(Figure 6).** To use microstructure array as a film form, the stage is made by spin-coating PDMS on glass and then attaching a spacer on the PDMS coated glass. In this case, polyimide tape was used as a spacer**.** Since it is necessary

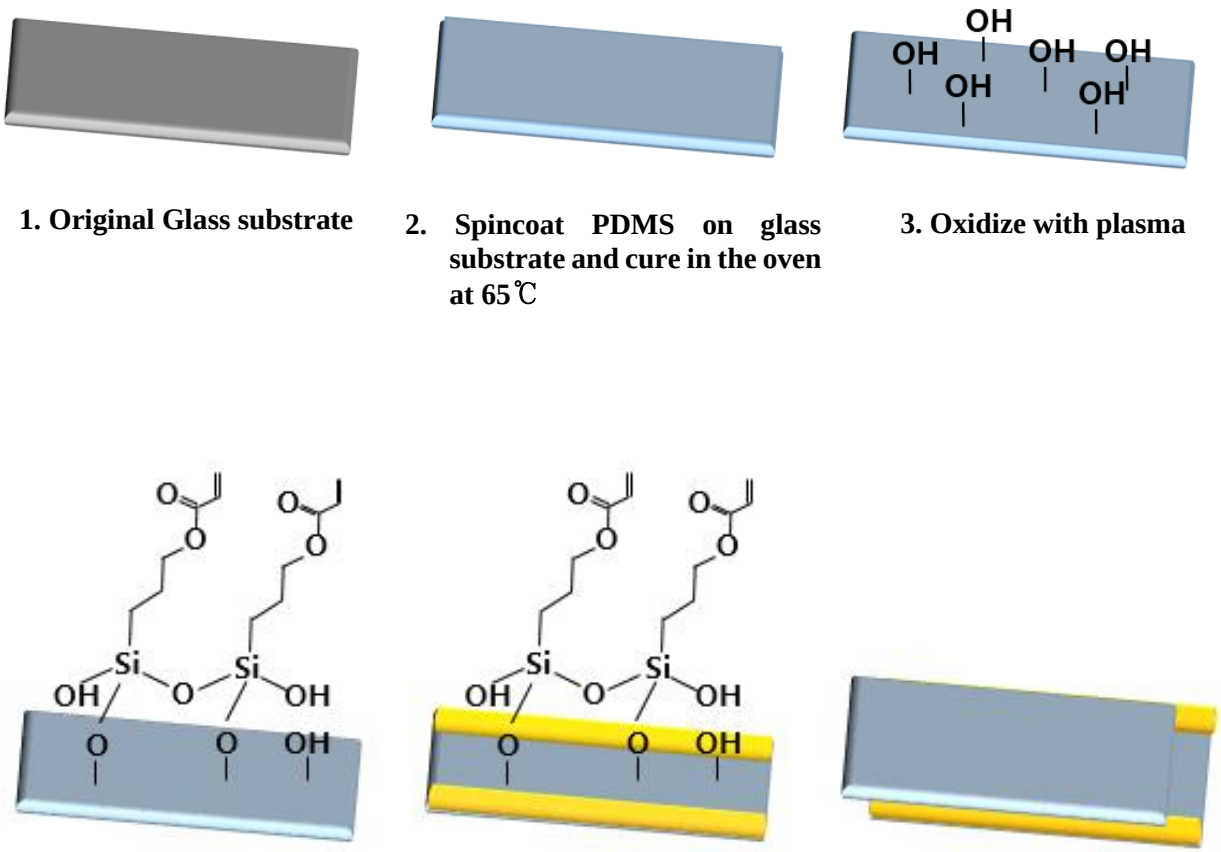
to construct and hold the structure, it is necessary to perform acrylate treatment using oxygen plasma**.** After fabricating Microstructure array stage, we inject UV-curable PDMS[42] to the stage, then exposed 365nm UV to the UV-curable resin using DMD based lithography system **(Figure 7).** After UV exposure, the residue is washed with ethanol. Because substrate is coated with acrylate reactive group, microstructures aren't washed but fixed on the PDMS substrate.

2.2.1 Micropost array fabrication

By adopting DMD based lithography system, various structure can be made by using photocurable resin. Micropost structure can be made by using circle-figured DMD light. If photocurable resin on the stage, is exposed by 365 nm UV light with a circle-figured DMD light, it become cross-linked and made into a post structure. Structure's height is determined depending on the height of the spacer. In this step, polyimide tape (130um thickness) was used as a spacer. Microstructure array can be made by fabricating micropost structure at regular intervals. (**Figure 8**).

2.2.2 Microdome fabrication

Several methods can be used to improve the precision of shape in photolithography. We report a patterning approach utilizing DMD-based grayscale lithography. Because DMD-based lithography system can change projection pattern, grayscale projection is also possible in lithography system. This type of lithography can improve fabrication accuracy for three-dimensional structure. Using grayscale lithography, we can expose gradient UV radiation to a photocurable resin. Gray scale adjust light gradation. By adjusting the brightness of the gray scale lithography, we can control the fine shape of the structure. In the circular light pattern, the transmittance of light increases as it goes from the outside to the center[43-44] **(Figure 9(a)).** Since the photocurable resin is cured as much as the light is transmitted, we can create dome-like structure depending on the amount of gradated light **(Figure 9(b)).** We can change the degree of gradient from the center to the outside. By choosing any desired gradient via gray scale lithography, we can fabricate any desired structure. As the change in the brightness to the central portion becomes more severe, the structure becomes a cone structure rather than a dome structure. By adjusting the light exposure time and focal point of light, we can control the shape of the structure precisely **(Figure 9(c), 9(d)).** Even if the height of the stage is fixed, the height of the structure does not grow by the height of the stage. As the light exposure time increases, the height of the structure increases. By setting the focal point of the light where it is, fabricated structure is also changed. By changing these variables, desired structure can be fabricated.



1. Original Glass substrate

2. Spincoat PDMS on glass substrate and cure in the oven at 65℃

3. Oxidize with plasma

4. Surface activation with 3-(trimethoxysilyl) propyl acrylate (TSPA)

5. Attach the PDMS spacer

6. Attach the PDMS coated TOP glass

Figure 6. Microstructure array stage fabrication procedure

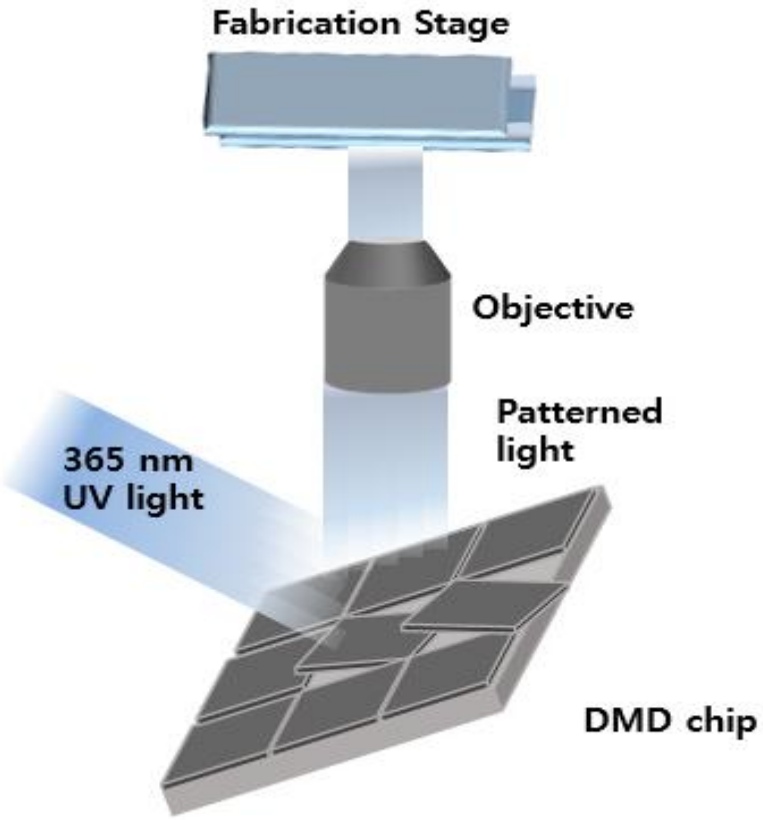


Figure 7. Scheme of DMD based microstructure array fabrication

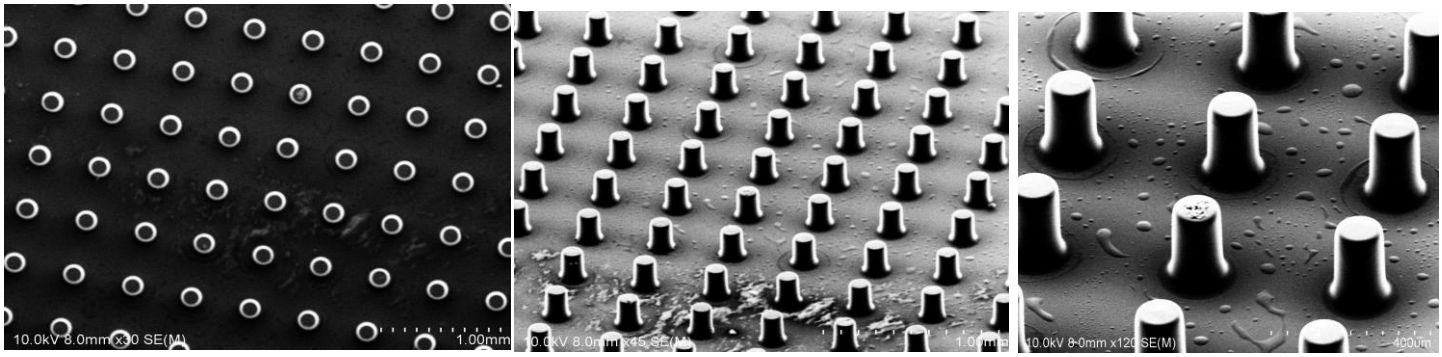


Figure 8. Micropost structure fabricated by DMD technique

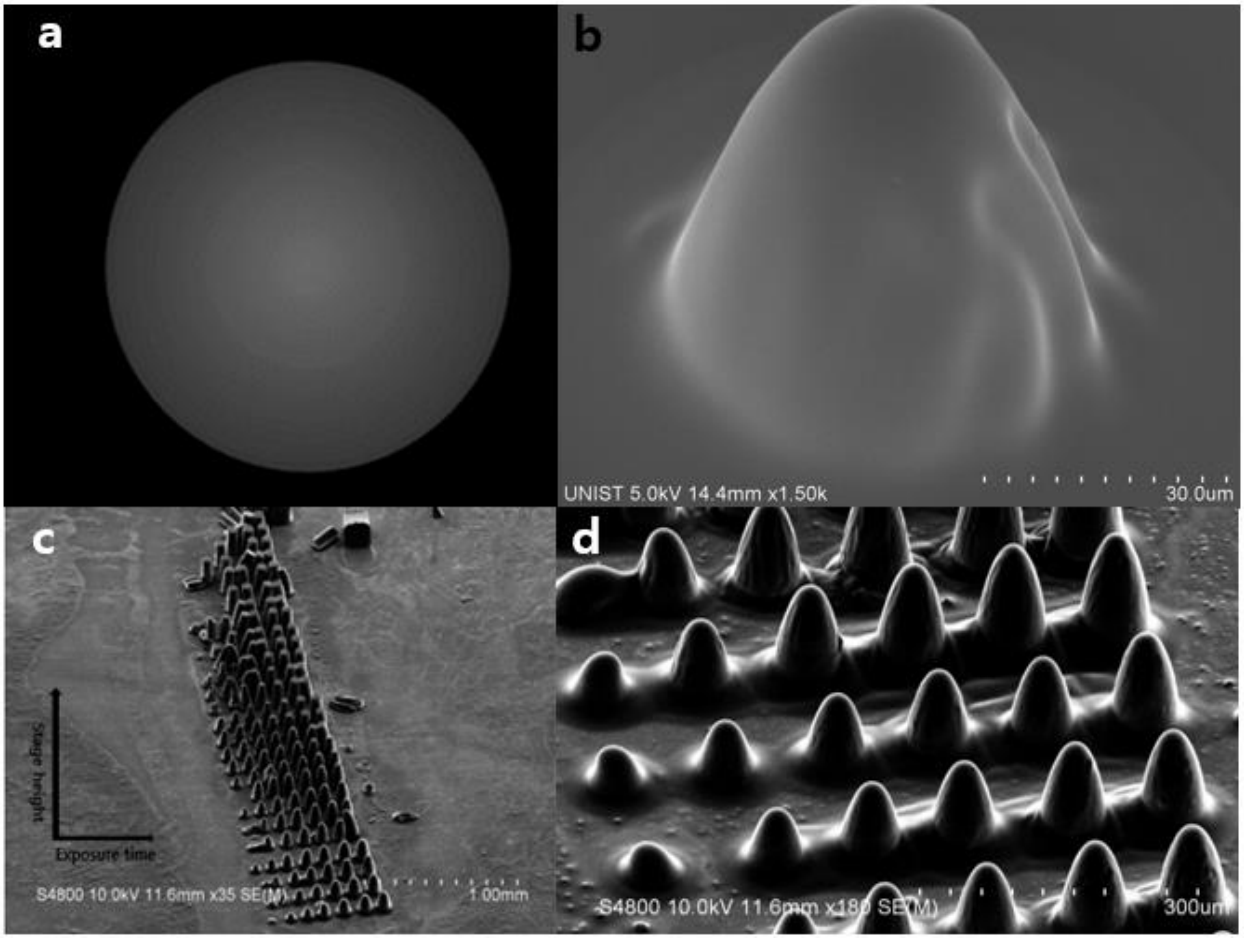


Figure 9. Grayscale lithography. Using (a) grayscale mask, we can expose gradient UV radiation to a photocurable resin. Gray scale adjust light gradation, and create not a micropost structure but a (b) microdome structure. By changing degree of gradient, structure becomes more a cone structure rather than a dome structure. (c), (d) Shape of microstructure can be changed depending on exposure time and focal point.

2.2.3 Limitation of Microstructure array fabrication using DMD

DMD based lithography is a useful technology to fabricate a 3D microstructure having a complex and high-aspect ratio since it is easy to modulate light radiation pattern. The disadvantage of our lithography platform using DMD is that it takes a long time to make arrays because each structure is taken one by one. When a large capacity microstructure array have to be fabricated in a short time, other methods are necessary.

2.3 Microstructure array fabrication using Contact lithography

We tried to fabricate microstructure array by using contact lithography platform. Contact lithography is a form of photolithography whereby the structure is obtained by illumination of a photomask in direct contact with a substrate containing a photocurable resin[45-46]. Depending on how the photomask is made, we can fabricate various structures and it can be used as high throughput lithography in short time. We made a custom designed high throughput photomask which is made of soda lime glass with a low reflective chrome pattern etched onto the surface. Since a mask must be prepared in advance to be used for micro-fabrication in contact lithography, various photomasks featuring circle, rectangle, square, are prepared in advance. This kind of lithography is suitable for microstructure array fabrication due to the fast process time using patterned light irradiation.

2.3.1 Microstructure array stage fabrication

To fabricate microstructure, stage should be made to be used as a substrate. We can fabricate microstructure on hard substrate like glass. But it can be used versatile if this is fabricated on soft substrate. We intended to form microstructure on flexible PDMS film. To use microstructure as film, Microstructure is fabricated on PDMS film. After spincoating PDMS on 5cm X 5cm glass, Cure the PDMS overnight in an oven at 65 °C[47]. Film thickness should be thick enough to detach from the glass and thickness determine film endurance. To achieve this, spincoating process is performed at low rpm. But too low rpm makes stage to be uneven, it is important to keep the thickness properly. Microstructure height is determined by spacer height. We made PDMS spacer using spincoating either. By regulating spincoating rpm, we can make different height of spacer which results in difference in microstructure's height. In this manner, the aspect ratio of microstructure can be adjusted by changing height of the spacer **(Figure 10).** The prepared spacers are applied to the PDMS-coated glass by oxygen plasma treatment[48-49]. After that surface will be treat with acrylate treatment. Stage is covered by top glass which is coated with PDMS. In low rpm spincoating,

PDMS is accumulated higher on the outside than on the middle. Because glass isn't flat if spin coating rpm is low, spincoating should be conducted at high rpm. Structures in **Figure 11(a)** and **Figure 11(b),** are made in the same experimental set. Structures in **Figure 11(a)** are fabricated on the middle part of the substrate and structures in **Figure 11(b)** are fabricated on the outermost side of the substrate. It can be seen that the height of fabricated structures is quite different depending on position in PDMS substrate. The top glass is also spincoated with a PDMS to prevent the microstructure from sticking to the glass. Top glass's flatness also affect the height distribution of the microstructure array. If the spincoating is conducted at low rpm in Top glass, height of the microstructure in middle region (**Figure 11(c)** would be different with height of the microstructure in outer region (**Figure 11(d).** But top glass may be thin enough because it wouldn't be used as a film. By spin coating at very high rpm, top glass can be very thin and minimize this phenomenon. **Figure 11(e)** shows microstructure array in inner region and **Figure 11(f)** shows microstructure array in outer region when top glass which is spincoated at high rpm, is used. There seems no difference in height distribution between them. By reducing the height of the structure, the durability of microstructure array during separating the PDMS film from the glass, can be greatly increased. Harder resins are easily damaged due to the modulus difference with the PDMS substrate. It can be solved by reducing the height and it results in reducing the stress on the structure. To prove it, HDDA resin with high modulus, was used as a photocurable resin for microfabrication. **In Figure 12,** polyimide tape with a 130um height, was used for micro-fabrication procedure. Using spacer with long spacer results in fabrication of high microstructures **(Figure 12(a)).** Such high structures are very susceptible to stress when spincoated and cured PDMS substrate are detached from glass **(Figure 12(b), (c), (d)). In Figure 12(e),** PDMS spacer with a 50um height, was used for micro-fabrication procedure which results in fabrication of relatively low-height structures. Low-height structures are relatively well tolerated by the stresses when the PDMS film is detached from the glass **(Figure 12(f), (g), (h)).**

2.3.2 UV exposure using Contact Lithography

To fabricate microstructure, we exposed 365nm UV to photocurable resin on the glass while fixing height by PDMS spacer. Depending on resin, its degree of curing is different so that we optimized each resin's UV power and exposure time. The estimated exposure time of each resin is tested and used during the fabrication. Both commercial photocurable resins, newly synthesized resin and blended resin can be used for improving the curing characteristics and mechanical properties

2.3.2.1 PUA- UV exposure using Contact Lithography

We used Polyurethane acrylate resin (MINS-311RM, Minuta Technology Co, Ltd) for contact lithography. It is usually used for stamp manufacturing of UV imprint, and it shows smooth releasing property and pattern transferring property in photolithography. It exhibits stable performance at pattern heights of micrometer scale. It is a UV curable material that is cured at the UVA wavelength band (400nm ~ 320nm). It also has hydrophobic character. To fabricate the PUA structure on a PDMS substrate, PUA which is mixed with photoinitiater as ratio of 9:1, is dropped onto the fabricated lithography stage. It is then cured by exposure to 0.8W of 365nm UV through a photo-mask for 250ms. After UV curing, the Top glass with PDMS substrate is removed from the stage, and then substrate is washed with ethanol **(Figure 13(a)).** Cured PUA shows characteristics of high modulus.

2.3.2.2. PEGDA- UV exposure using Contact Lithography

We also used PEGDA (PEGDA 700, Sigma-Aldrich) resin for contact lithography. It is a UV curable material that is cured at the UVA wavelength band. It also has hydrophilic character. To fabricate the PEGDA structure on a PDMS substrate, PEGDA which is mixed with photoinitiater as ratio of 9:1, is dropped onto the fabricated lithography stage. It is then cured by exposure to 0.8W of 365nm UV through a photo-mask for 150ms. Because it has two acrylate reactive group, exposure time is shorter to form microstructure compared to PUA. After UV curing, the Top glass with PDMS substrate is removed from the stage, and then substrate is washed with ethanol (**Figure 13(b)**). Cured PEGDA shows characteristics of flexibility.

2.3.2.3. HDDA- UV exposure using Contact Lithography

We also used HDDA resin (purchased from sigma Aldrich) for contact lithography. It is a UV curable material. To fabricate the HDDA structure on a PDMS substrate, HDDA which is mixed with photoinitiater as ratio of 9:1, is dropped onto the fabricated lithography stage. It is then cured by exposure to 0.8W of 365nm UV through a photo-mask for 150ms. Because it has two acrylate reactive group, exposure time is

shorter to form microstructure compared to PUA. After UV curing, the Top glass with PDMS substrate is removed from the stage, and then substrate is washed with ethanol. (**Figure 13(c)**)

2.3.2.4 PU- UV exposure using Contact Lithography

We also synthesized flexible Polyurethane resin and tested its property[50] and used this in contact lithography system. Polyurethanes are compounds which has structure of $[\text{-NHCOO-}]_n$ which is called as urethane bonds. This flexible PU resin also has urethane bonds with PTH as the primary chains, and it has acrylate reaction groups at both ends so that it can be used in photolithography. Since this resin has excellent characteristics of flexibility and elongation, it can be useful for fabrication of flexible microstructures in photolithography.

2.3.2.4.1 Synthesis of flexible PU resin

Flexible PU resin can be synthesized using urethane bonding. Urethane bonding refers to reacting an isocyanate group with hydroxyl group in the presence of some catalyst. For flexible PU resin synthesis, we used Isophorone diisocyanate (IPDI), poly(tetrahydrofuran) (PTH) for urethane bonding. Because PTH has a hydroxyl group at both ends, PTH is a chemical compound frequently used in the polyurethane manufacturing process. Since IPDI have two isocyanate groups, continuous reaction with PTH is possible. Various material can be used as catalyst and we used dibutyltin dilaurate as a catalyst in this reaction. If we put hydroxyl terminated PTH and IPDI with isocyanate functional group, isocyanate group reacts with the hydroxyl group to form a urethane bond and the mixture forms long chain. After long chains of polymer is formed, mixture of 2-hydroxyethyl acrylate 2-Methyl-1-propanol, are added. It results in attaching acrylate functional groups on both ends of the chain and 2-methyl-1-propanol terminated polymerization **(Figure 14).** Long chains help to be a soft elastomer and many bonding helps to be a hard polymer. Maintaining a balance between them, can make a very elastic polymer with rigidity[51].

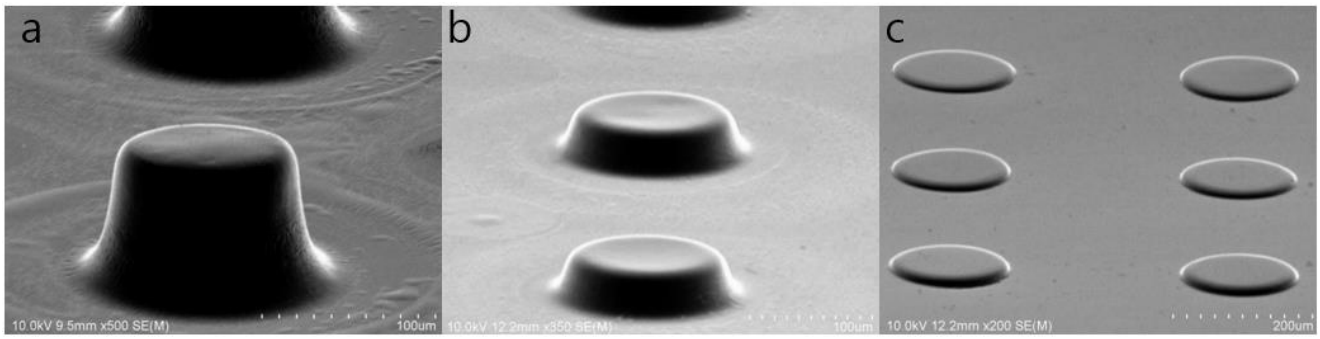


Figure 10. Height control of microstructure changing the height of PDMS spacer (a) 100um (b) 50um (c) 25um

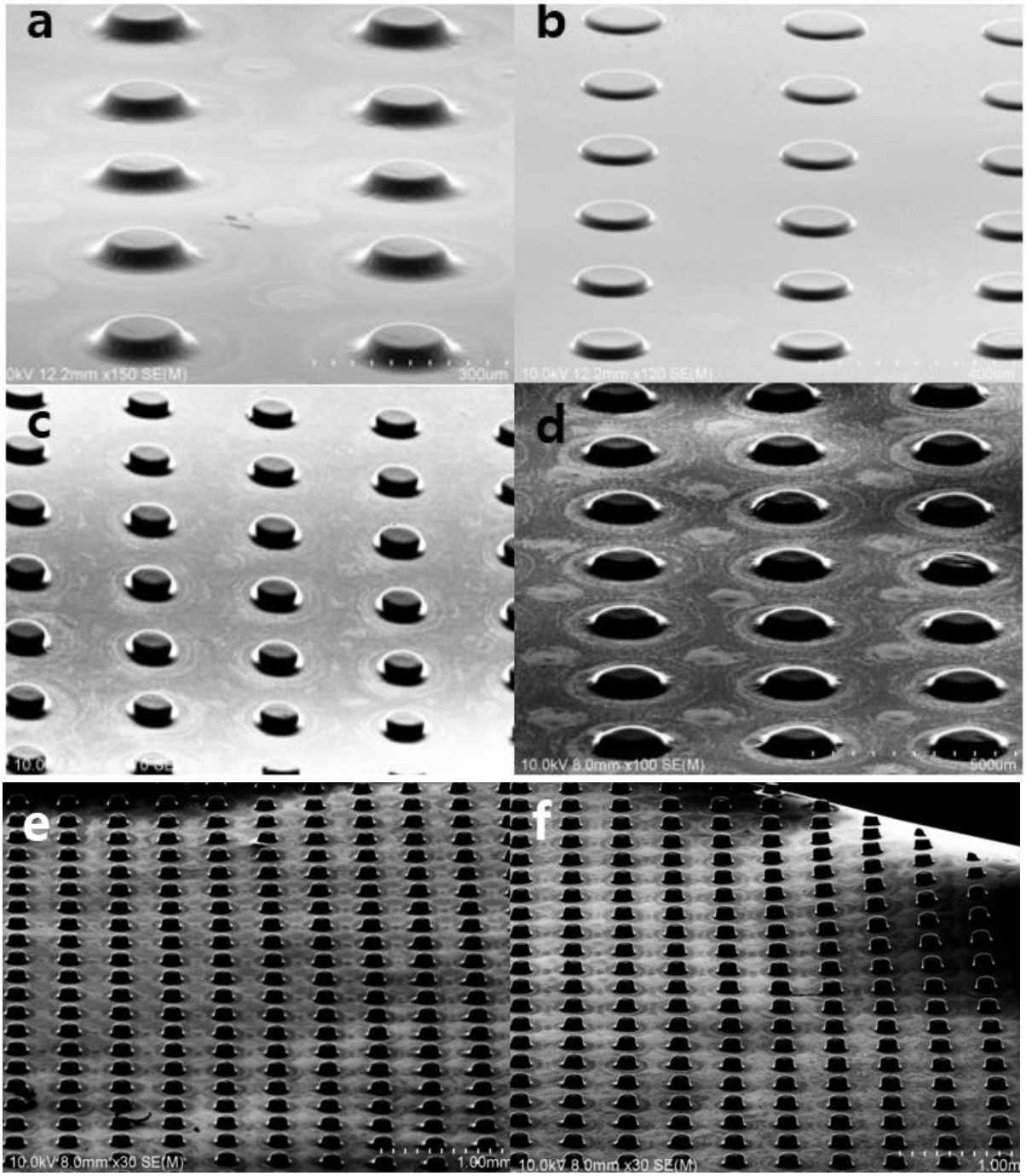


Figure 11. PDMS spin coating dependence on flatness. Structures in Figure (a) and Figure (b) are made in the same experimental set. Structures in Figure (a) are fabricated on the middle part of the substrate and structures in Figure (b) are fabricated on the outermost side of the substrate. Figure (c) and Figure (d) shows microstructure distribution when top glass which is spincoated at low rpm, is used. Figure (e) and Figure (f) shows microstructure distribution when top glass which is spincoated at high rpm, is used.

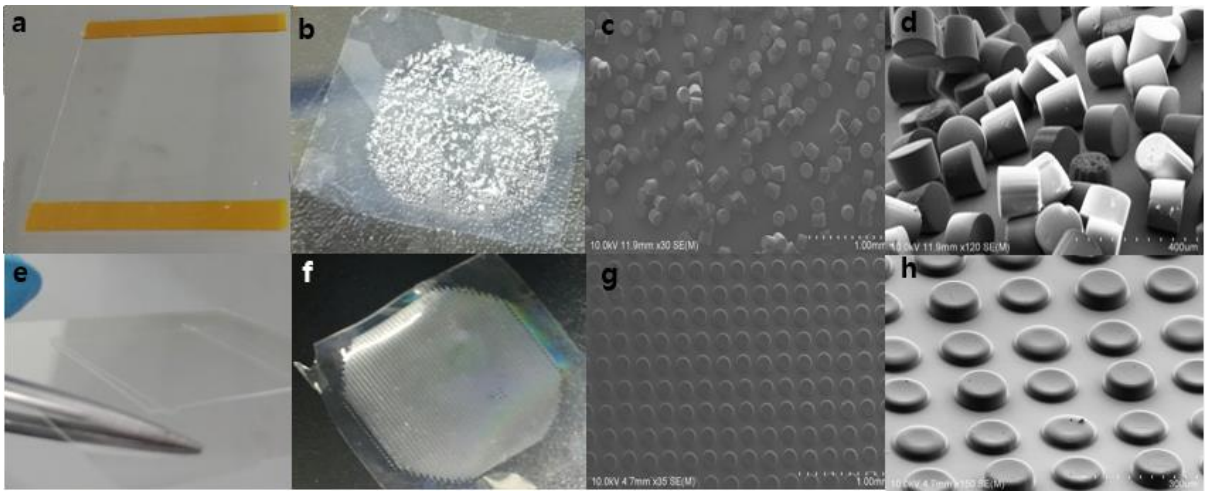


Figure 12. Difference in durability of HDDA depending on height. For figure a, b, c, d, the microstructure is made from a 150um spacer. For Figure e, f, g, h, the microstructure is made from a 50um spacer. Figure (a), (e) shows that different spacer is used in the microstructure fabrication. Figure (b), (f) is the image of film after detaching the film from the glass. Figure (c), (d) is the SEM image when a high spacer is used, Figure (g), (f) is the SEM image when a low spacer is used

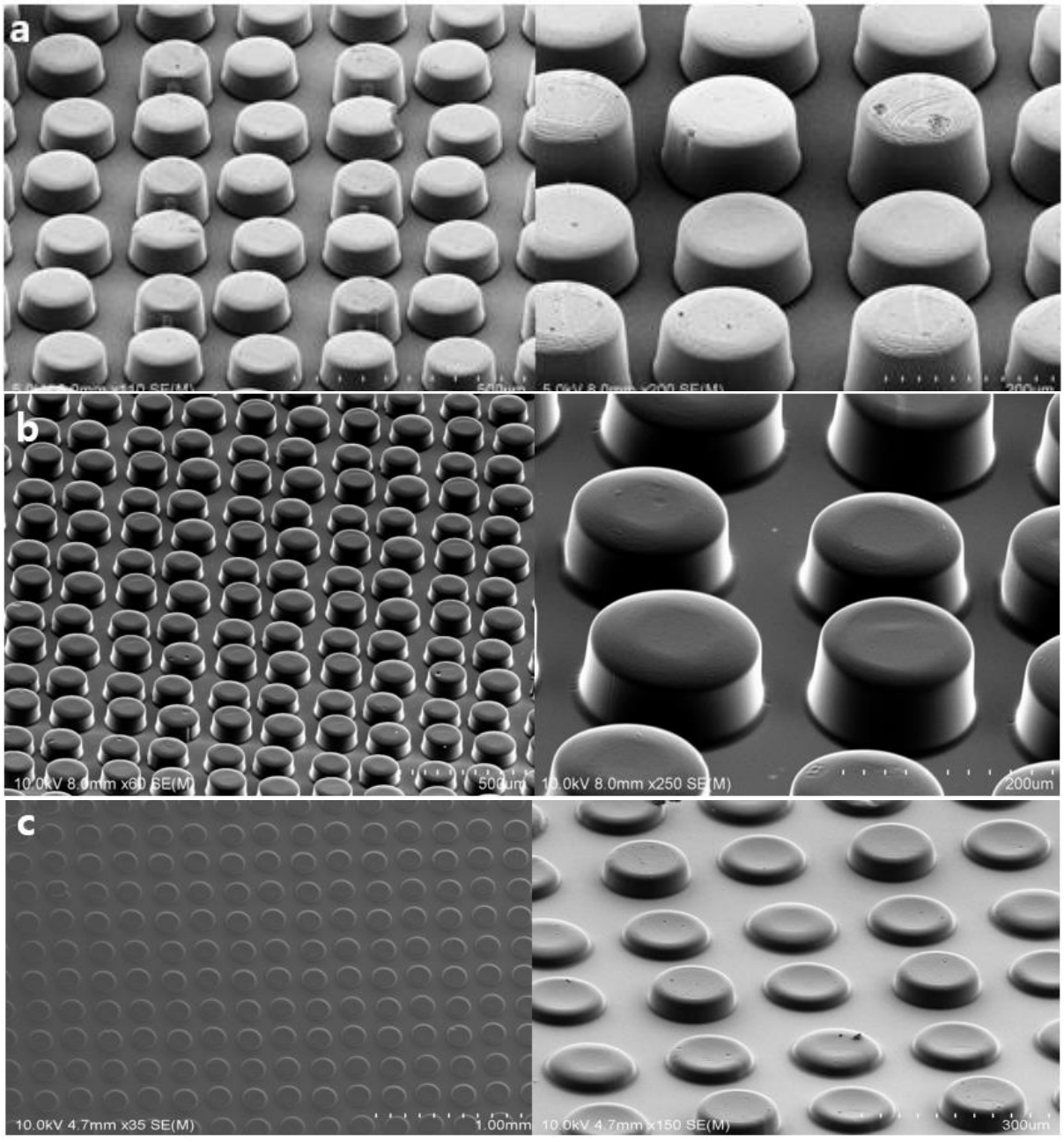


Figure 13. Microstructure array fabricated by contact lithography for (a) PUA resin (b) PEGDA resin (c) HDDA resin

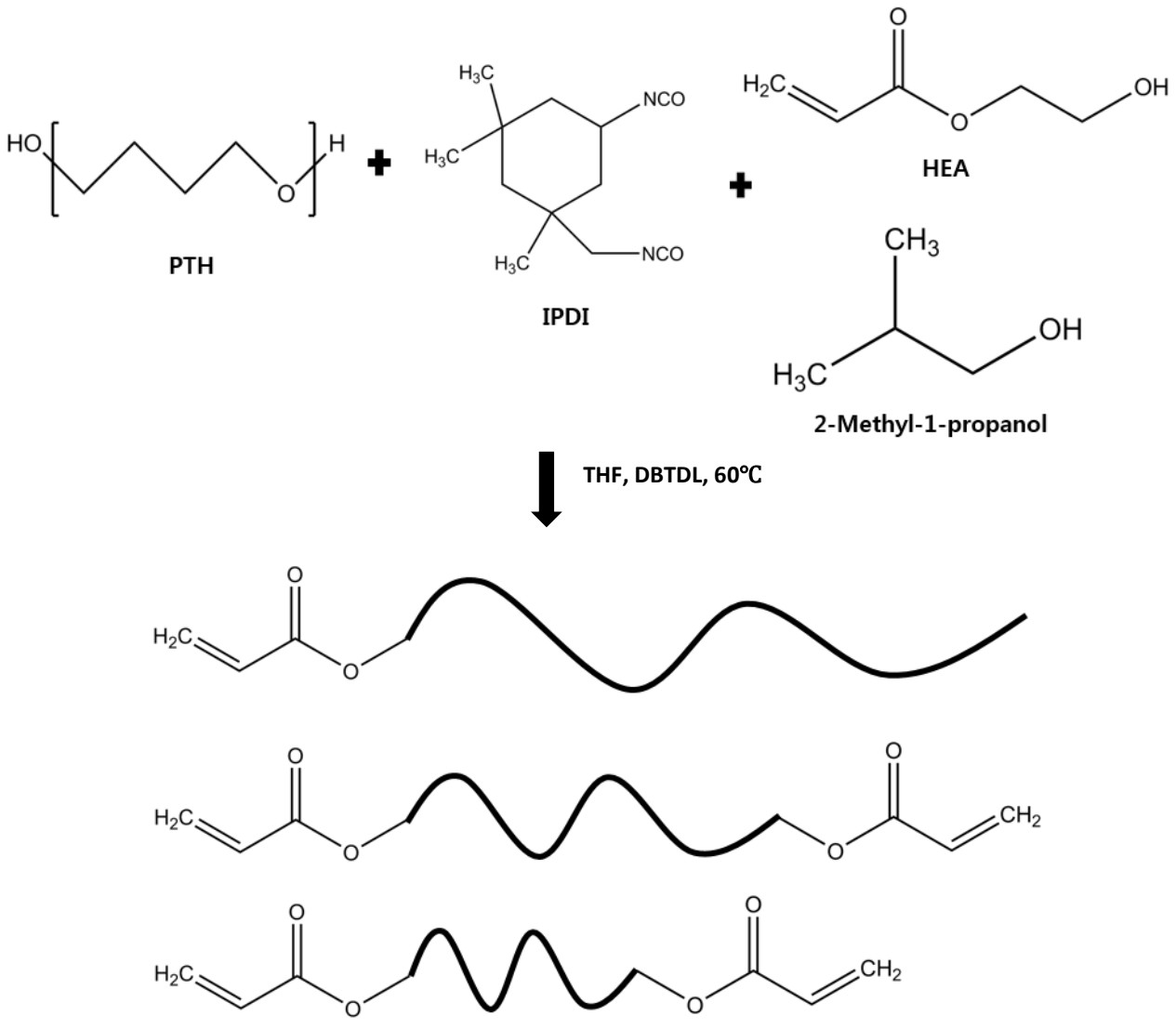


Figure 14. Flexible PU resin synthesis scheme

2.3.2.4.2 Characteristics and Importance of flexible PU resin

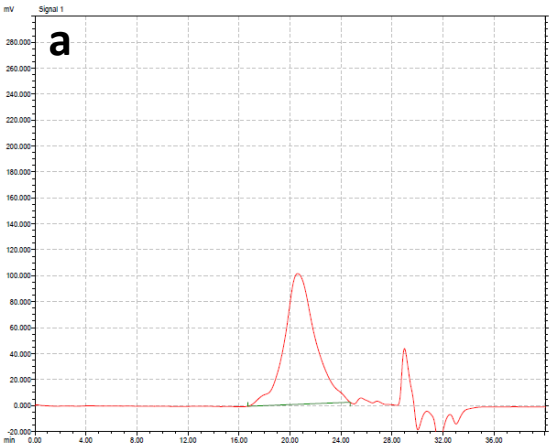
Continuous urethane bonds form a long polymer network, which results in too high viscosity which makes it hard to be used in lithography. Because low molecular weight and wide polydispersity of resin can decrease its viscosity, in which the low molecular weight chains can be used as diluents, we let the reaction proceeds at a low temperature of 60 ° C to form a low molecular weight polymer with wide polydispersity which results in low viscosity to be handled (**Figure 15 (a))**. This resins do not dissolve in water, but dissolve well in a series of alcohol like ethanol or IPA. This resin is hardened by UV at high speed and has characteristics of flexibility and elongation when it became cross-linked. Film with 300um of thickness, is increased to about 650% (**Figure 15 (b), (c), (d))**. Because it has characteristics of flexibility and elongation this resin can be used in various way.

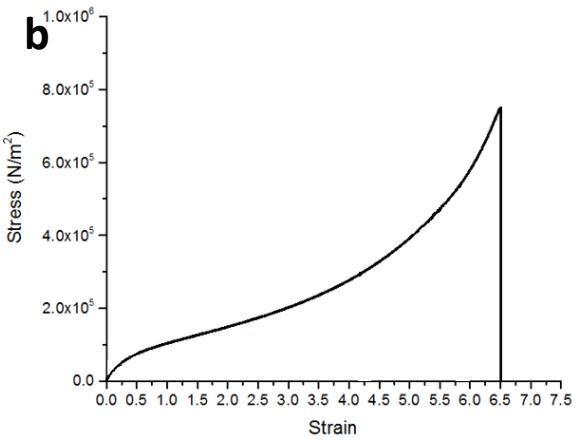
2.3.2.4.3 PU- UV exposure using Contact Lithography

Because this resin has high viscosity and there is a limit to reducing viscosity by controlling reaction temperature, we have to use this by mixing other photocurable resin. 3-trimethoxysilylpropyl acrylate, PEGDA, PUA were applied to flexible PU and photolithography procedure. To fabricate the PU blend structure on a PDMS substrate, PU is mixed with each resin and photoinitiater. Solution is injected to the fabricated lithography stage. It is then cured by exposure to 365nm UV through a photo-mask. After UV curing, the Top glass with PDMS substrate is removed from the stage, then substrate is washed with ethanol, and microstructure array can be obtained. In case of blend structure with 3-trimethoxysilylpropyl acrylate, we can get normal microstructure (**Figure 16(a))**. When flexible PU resin was mixed with PEGDA, large pores were formed in the structure (**Figure 16(b))**. When flexible PU resin was mixed with PUA, microstructures were easily damaged since PUA is a high modulus resin which results in modulus difference between PDMS substrate. (**Figure 16(c))**.

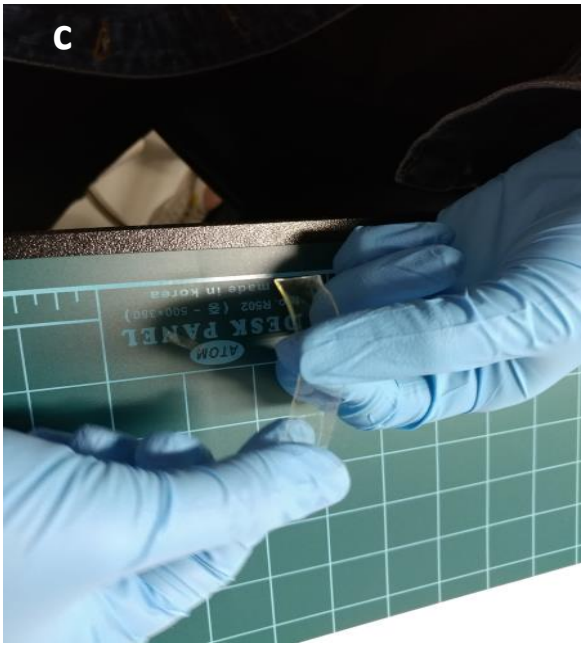
2.4 Microstructure array – mechanical property

Because structure is fabricated on PDMS substrate. Elastic modulus difference between fabricated structure and PDMS substrate, heavily affects with its endurance. Depending on which resin is used, the durability of the structure is determined. Even if durability of microstructure array is increased by reducing the height of the structure, originally hard resin like PUA, has a limit of durability compared to the flexible resin like PEGDA. During detaching the film from glass substrate, microstructures made of PUA resin lost its structure (**Figure 17(a)**). On the other hand, microstructures made of PEGDA aren't damaged (**Figure 17(b)**).





Mn = 11382 Mw/Mn = 2.595
Mw = 29536



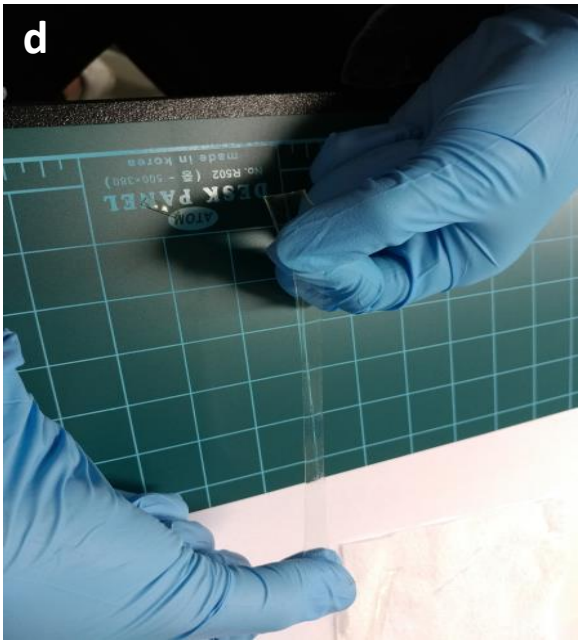


Figure 15. Characteristics of flexible PU. (a) GPC data of flexible PU, Elongation property of flexible PU. (b) Film can be stretched to 650%. Image of film (c) before (d) after stretched.

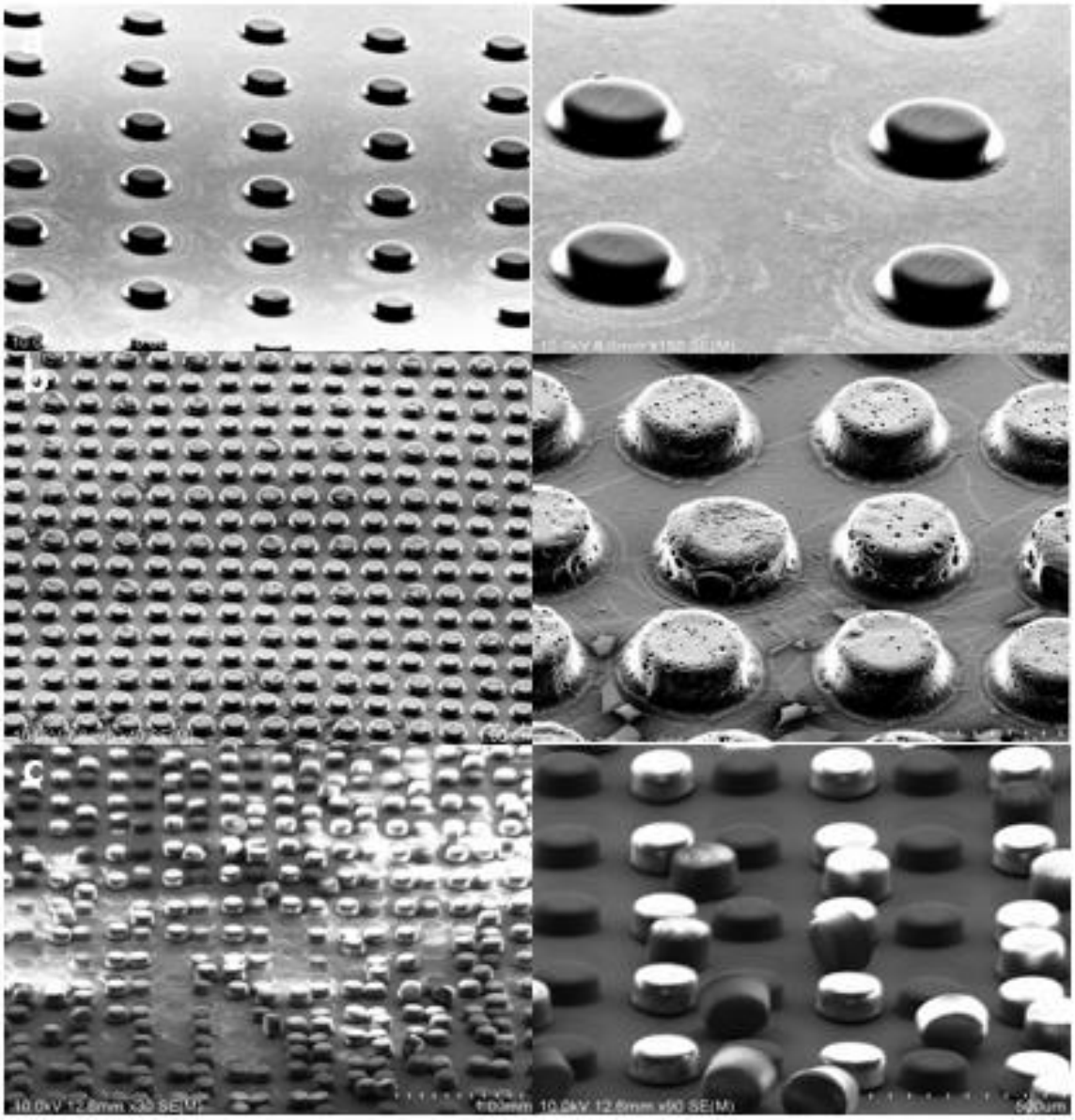


Figure 16. PU blend structure fabricated by contact lithography. Microstructure made of flexible PU resin with (a) 3-trimethoxysilylpropyl acrylate, (b) PEGDA, (C) PUA

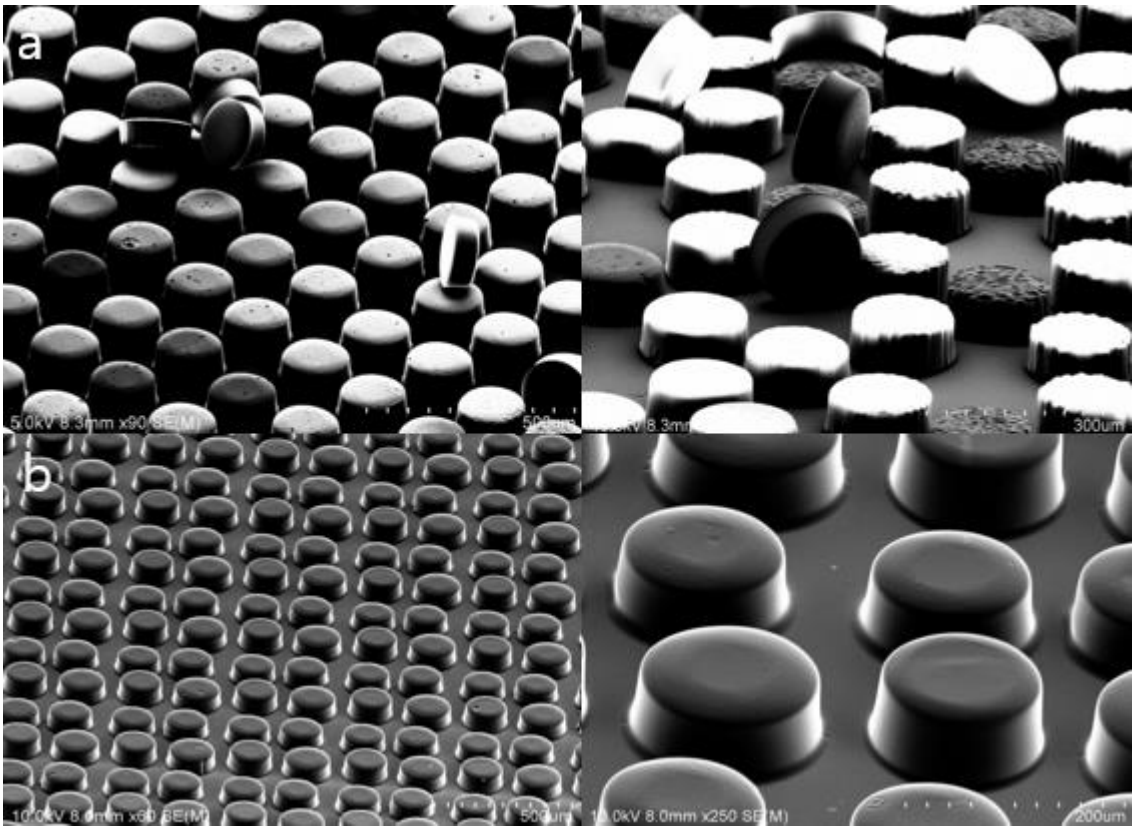


Figure 17. Endurance difference of microstructure array depending on modulus of resin. (a) PUA structure is easily damaged by stress because of its modulus difference between PDMS substrate. On the other hand, (b) PEGDA structure can maintain its structure

3. UCN based Microstructure array fabrication

We presents a new type of microstructure array which consists of Upconverting Nanocrystals (UCNs). Upconverting nanocrystal (UCNs) are lanthanide doped nano-size crystal, which can be excited with near infrared (NIR) light at a single wavelength and radiates visible light for anti-Stokes fluorescence[51-54]. By adopting UCNs, it is possible to create a new concept of microstructure array that respond to near-infrared rays. By using not a just photocurable solution but a UCN dispersed photocurable resin, we can fabricate UCNs contained structure. Then by using ethanol, wash the stage to remove unpolymerized resin. Then we can fabricate final result of UCN contained microstructure array,

3.1. UCN synthesis

In this work, hexagonal phase rod shaped crystal doped with upconverting lanthanide ions (Er^{3+}, Yb^{3+},Tm^{3+}) was synthesized by hydrothermal method. $NaYF_4$ was chosen as the host material because it is known as one of the best host materials for upconverting lanthanide ions[55]. When doping Yb^{3+}, Er^{3+} and Tm^{3+} ions into $NaYF_4$ nanocrystal and $Gd^{3+}$is codoped for phase control of crystal, the efficiency of upconversion luminescence is much higher than luminescence for other phase of nanocrystal such as cubic phase. By regulating ratio of lanthanide dopants such as Yb^{3+}, Er^{3+} and Tm^{3+}, we synthesized various color of UCNs. **Figure 18(a)** is the SEM image of synthesized UCNs which shows hexagonal phase of UCNs in rod shape. **Figure 18(b)** shows optical images of red, green, blue, yellow UCNs irradiated by 980nm NIR. **Figure 18(c)** is spectrum of each color. UCN's color is determined by combination of specific wavebands including 660nm, 550nm, 480nm.

3.2 UCN surface modification and dispersion in photocurable resin

Based on our recipe of UCN synthesis, we synthesized long rod-shaped UCNs capped in oleic acid through a hydrothermal reaction. Because crystal surface was capped by hydrophobic oleic acid, it results in hydrophobicity of UCNs. Hydrophobicity of crystal disturb dispersion quality of UCNs with various kinds of resin. To overcome this, several surface modification methods have been developed[56-59]. By using surface modification methods, we can modify surface chemistry of nanocrystal in various way.

3.2.1 UCN dispersion in hydrophobic PUA

To disperse UCNs with hydrophobic PUA (MINS311RM), we need to know surface chemistries of oleic acid capped UCNs with hydrophobic PUA. Because UCN surface is coated with hydrophobic oleic acid, its surface chemistry allows homogeneous dispersion quality with hydrophobic PUA. UCN's rod-like structure also assists in the homogeneous dispersion with PUA structure. Sonication makes UCNs dispersed with blend of PUA monomer and photo-initiator easily. Uniformly dispersed solution can be used in Micro-fabrication.

3.2.2 UCN oxidation and dispersion in hydrophilic PEGDA

In contrast, dispersion with PEGDA, requires hydrophilic surface chemistry. At first, we synthesized rod-like UCNs capped in oleic acid through a hydrothermal reaction and then hydrophilic UCNs were formed by oxidation procedure which results in excellent dispersion in blend of PEGDA and photo-initiator.

3.2.2.1 UCN oxidation

Oxidation of UCNs was conducted by using Lemieux-von Rudloff reagent[60]. Lemieux-von Rudloff reagent oxidized double bonds of oleic acid ligands in UCNs, and it results in formation of hydrophilic carboxylate groups on the surface of UCNs, enabling UCNs dispersed in hydrophilic polymer.

3.2.2.2 Oxidized UCN dispersion in hydrophilic PEGDA

Because all single crystals aren't oxidized perfectly, dispersion property isn't perfect with PEGDA. To overcome that, additive Polystyrenesurfonate (PSS) is used. By adding PSS, the dispersion quality is greatly improved. After oxidized UCNs and PSS are dropped onto PEGDA, then it is mixed by ultrasonication. These UCNs can be dispersed well in a blend of PEGDA monomer and photo-initiator to be used in Micro-fabrication (**Figure 19**).

3.2.3 UCN silica coating and dispersion in flexible PUA

Because application of hydrophobic oleic acid capped UCNs is limited due to its dispersion property with various solvents or polymer, several surface modification methods have been developed to increase

dispersion property of nanoparticle. Surface of nanoparticle have to be modified depending on solvents or polymer to be dispersed. To disperse UCNs with flexible PUA, we have to consider dispersion chemistry of this polymer with solvents. Flexible PU isn't totally dissolved in water, but can be dissolved in Ethanol, methanol etc. we could coat silica with UCNs. In order to utilize the property of flexible PUA to be dissolved in ethanol, we also used surface chemistry of UCNs to make it soluble in ethanol. Because silica coating exhibits excellent dispersion property in solvents such as ethanol, methanol, UCNs were coated with thin silica[61].

3.2.3.1 UCN silica coating

First, the uniform hexagonal phase rod-like UCNs capped with hydrophobic oleic acid ligand were synthesized by the hydrothermal method. And then they were modified by amphiphilic nonionic surfactant Triton X-100. Oleic acid ligand reacts with Triton X-100 solution and forms hydrophilic surface. Next, the modified nanocrystals were coated thinly with a silica layer through St€ober method which is a chemical process used to make controllable silica particles with uniform size. It forms hexagonal phase rod shaped UCNs coated with thin silica layer (**Figure 20(a)**). Because it is encapsulated by silica layer, it exhibits similar surface chemistry with silica nanoparticle.

3.2.3.2 Silica coated UCNs dispersion in flexible PUA

Considering that flexible PU is soluble in ethanol, silica coated UCNs dispersed in ethanol would be used in dispersion and micro-fabrication procedure. Silica coated UCNs dispersed in ethanol, are added to the flexible PU solution and ultrasonication is used to disperse them in polymer. Ultrasonic treatment must be useful for nanoparticle dispersion. But it is still considered that longer ultrasonic treatment time will result in particle clustering due to charge accumulation. **Figure 20(b)** shows the dispersion image of silica coated UCNs in flexible PU and **Figure 20(c)** shows the dispersion image of silica coated UCNs in blend of flexible PU and 3-trimethoxysilylpropyl acrylate. Both Images taken under 980 nm continuous-wave laser. The dispersion degree increases depending on which resin is used. By changing the resin, dispersion quality of resin is changed. Therefore silica coating can be used to improve the dispersion quality.

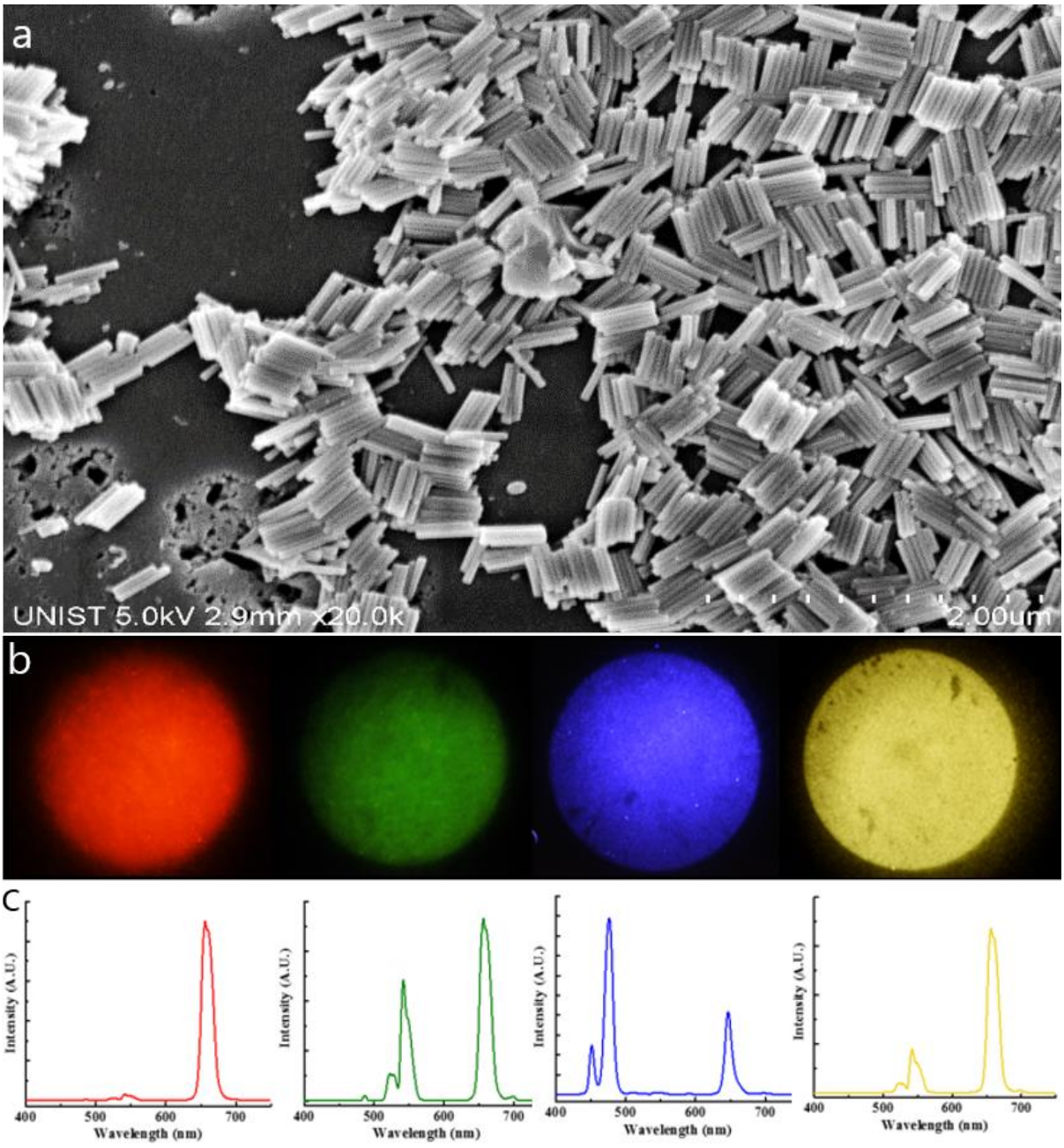


Figure 18. Rod-shape UCNs were synsthesized. (a) SEM image of rod shape UCNs (b) Optical images of UCNs ranging from red, green, blue, yellow taken under 980nm continuous-wave laser (C) Spectrum for UCNs ranging from red, green, blue, yellow

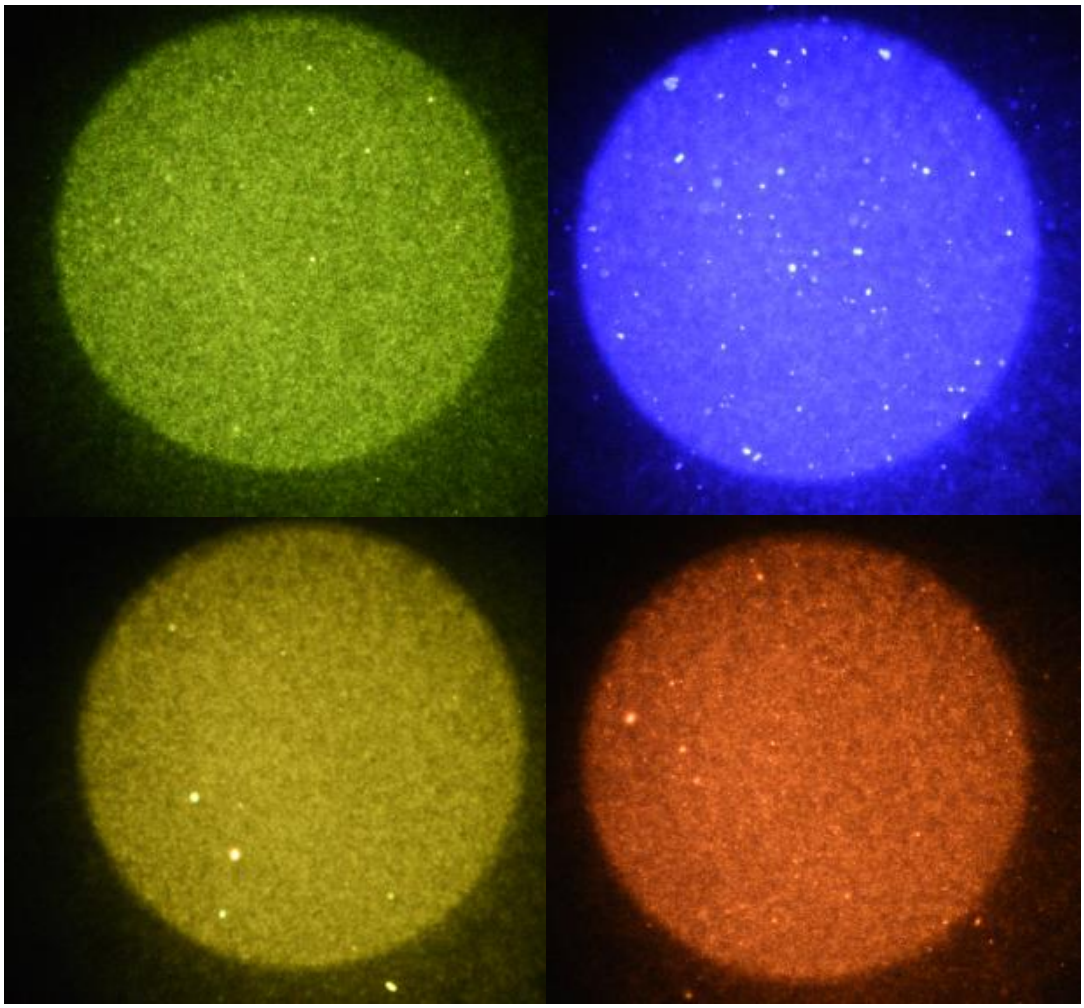


Figure 19. Dispersion image of oxidized UCNs in PEGDA. Image of green, blue, yellow, red UCNs were taken under 980 nm continuous-wave laser

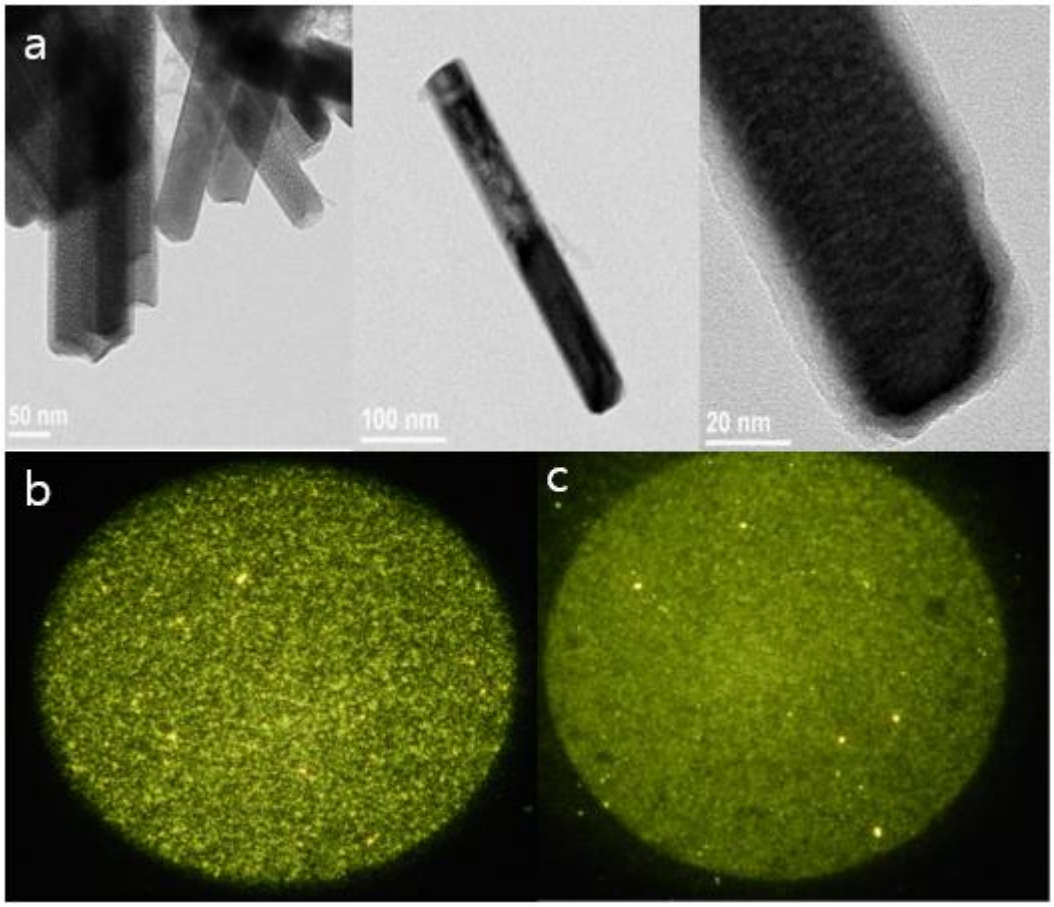


Figure 20. Silica coated UCNs. (a) TEM image of silica coated UCNs (b) Dispersion image of silica coated UCNs in flexible PUA (c) Dispersion image of silica coated UCNs in blend of flexible PUA and 3-trimethoxysilylpropyl acrylate. Silica coating affects dispersion quality depending on which resin is used. Both images taken under 980 nm continuous-wave laser

3.3 UV exposure on UCN dispersed solution

UCN integrated microstructure array is manufactured in the same manner as a microstructure array that doesn't contain UCNs. After dispersing UCNS with photocurable resin, it is mixed with photoinitiators. UCNs dispersed solution is injected to fabricated microstructure array stage. Then UV is exposed to stage, then microstructure can be fabricated resulting from crosslinking. For additional structure fabrication, stage is washed with ethanol and then same steps are repeated.

3.3.1. Nonspecific binding of UCNs with PDMS surface.

After UCNs synthesis of specific color, surface of UCNs have to be treated according to the physical properties of the polymer to be cured. During synthesis, hydrophobic oleic acid is used as a capping agent. Because of that, PUA and other hydrophobic resins don't require additional surface treatment. After dispersing normal UCNs with PUA resin by ultrasonication, solution is mixed with photoinitiator. UCN dispersed solution is injected to fabricated microstructure array stage then UV is exposed to the stage containing solution. Then UCN dispersed microstructure can be fabricated. Remaining solution is washed with washing solvent. We used ethanol as a washing solvent. If normal UCN is used at this time, the UCN is not washed well, and it is difficult to obtain a clean microstructure array (**Figure 21(a)**). Inhomogeneous color distribution happens occur due to non-specific interactions of oleic acid capped nanocrystal with the PDMS surface.

3.3.2 Multi color UV exposure using Contact Lithography

Because non-specific nanoparticles are accumulated across the stage, it is difficult to construct microstructure array using oleic capped UCNs. In the case of microstructure array of various colors, this should be avoided because the colors are mixed (**Figure 21(b)**). We have to use nanocrystal which can be washed easily with ethanol to prevent non-specific binding of nanoparticles with substrate. If we use oxidized UCNs or silica cotated UCNs, we can solve this problem. With surface-modified UCNs, microstructure array of various colors are made clean. (**Figure 22**). If additional microstructures are needed,

add the top glass after washing, inject the UCN dispersed solution again and expose the UV focusing the UV lens between the arrays. In this way, it is possible to produce microstructure array of various colors. Since the intensity of the UCNs isn't uniform by color, microstructure array of unbalanced colors is fabricated if concentration is not taken into account (**Figure 23**). It is necessary to measure the RGB value of the UCNs and then construct the structure after adjusting the concentration of each color (**Figure 24**). After all steps, PDMS film containing microstructure array dispersed with multi-color UCNs can be obtained. This kind of film respond to infrared rays and can be applied in various color combinations (**Figure 25).**

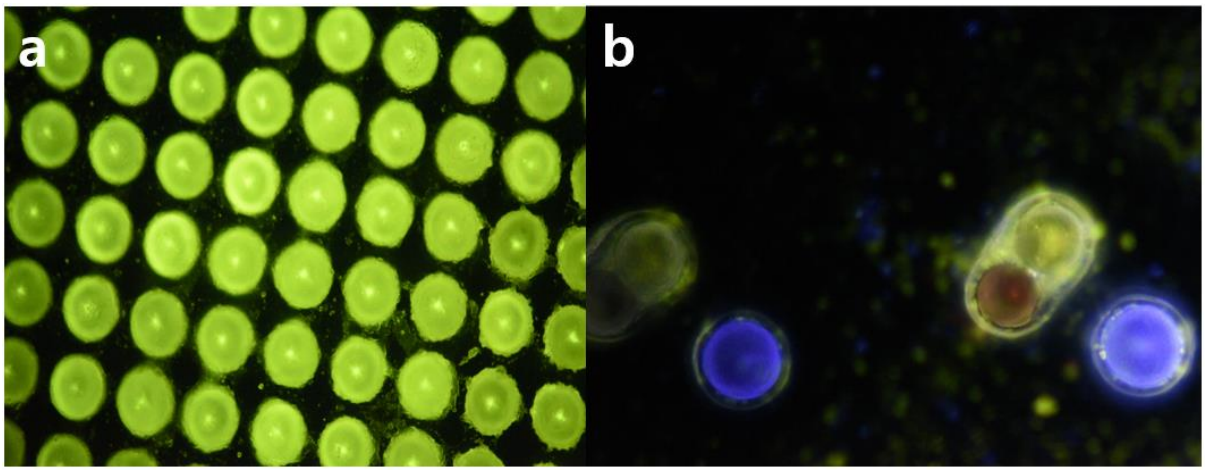


Figure 21. Nonspecific binding of oleic acid capped UCNs with PDMS substrate disturb clear distribution of (a) green microstructure array. (b) Multi-color microstructure array. Images taken under 980 nm continuous-wave laser.

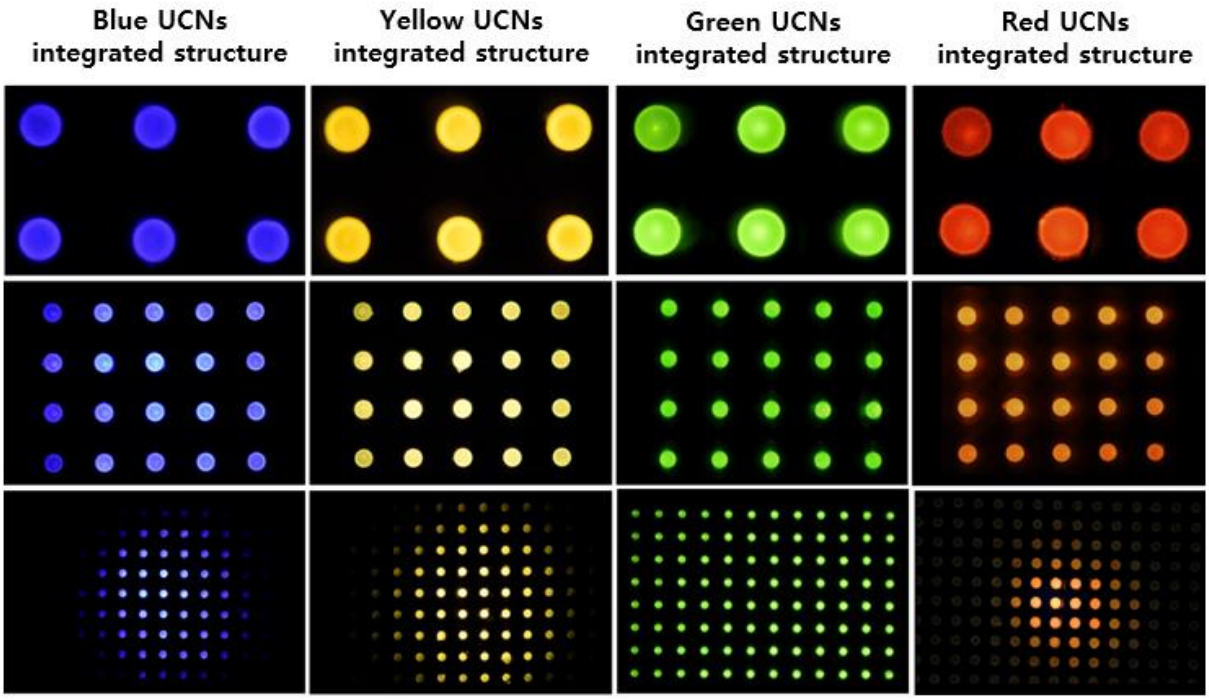


Figure 22. Optical images of one color microstructure array which contains silica coated UCNs; Images taken under 980 nm continuous-wave laser. Microstructure array of each color was made of UV-PDMS with silica coated UCNs by DMD based lithography. Images taken under 980 nm continuous-wave laser.

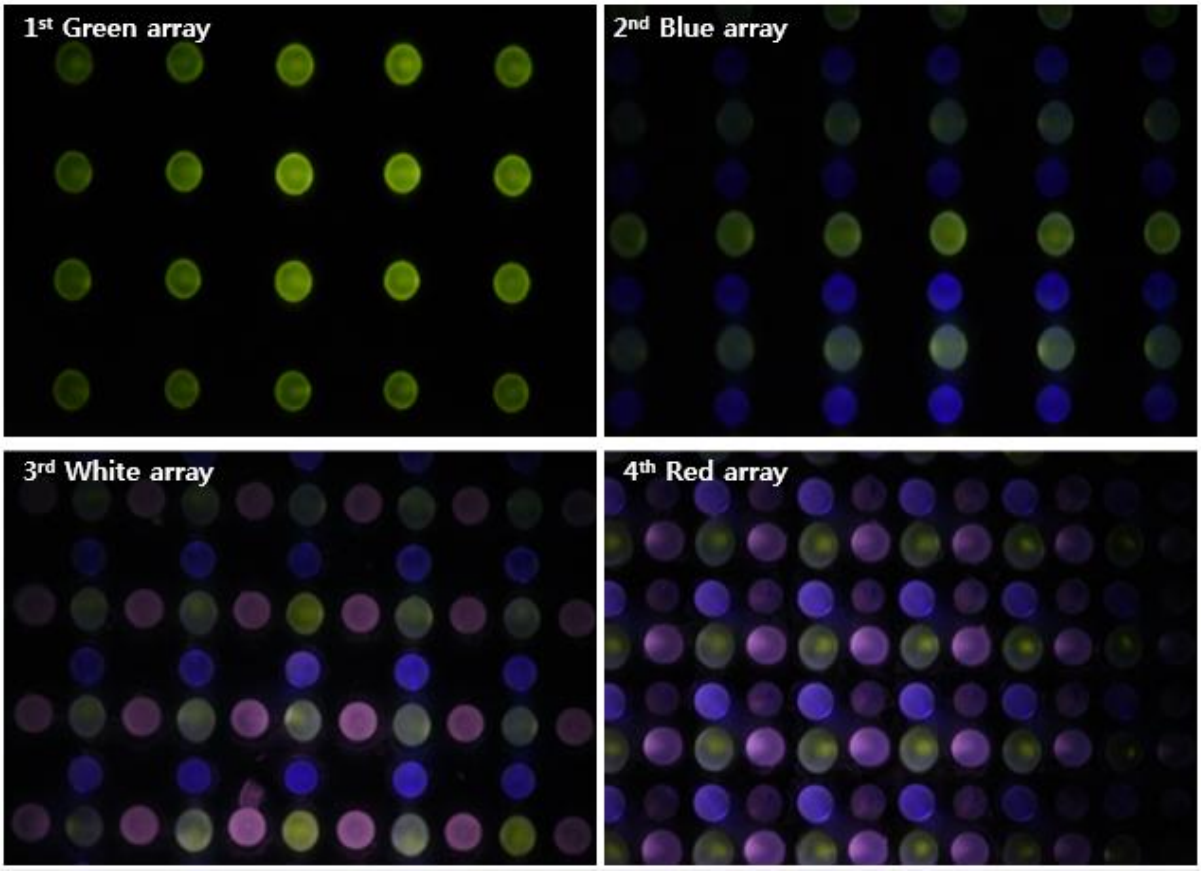


Figure 23. Multi-color microstructure array fabrication procedure in which the concentration balance of silica coated UCNs is not controlled. Green array, blue array, white array, red array were made in order. Microstructure array was made of UV-PDMS with silica coated UCNs by DMD based lithography. Images taken under 980 nm continuous-wave laser.

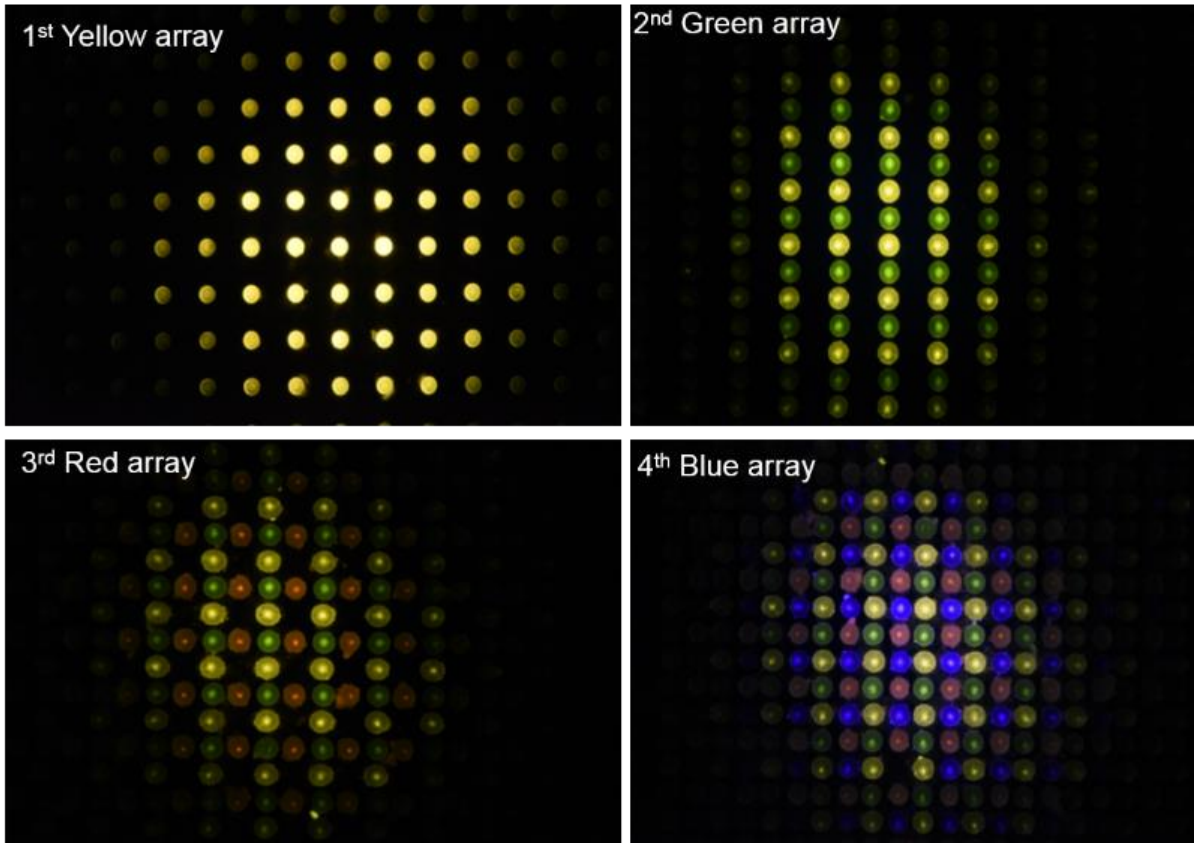


Figure 24. Multi-color microstructure array fabrication procedure in which the concentration balance of silica coated UCNs is controlled. Yellow array, green array, red array, blue array were made in order. Microstructure array was made of UV-PDMS with silica coated UCNs by DMD based lithography. Images taken under 980 nm continuous-wave laser

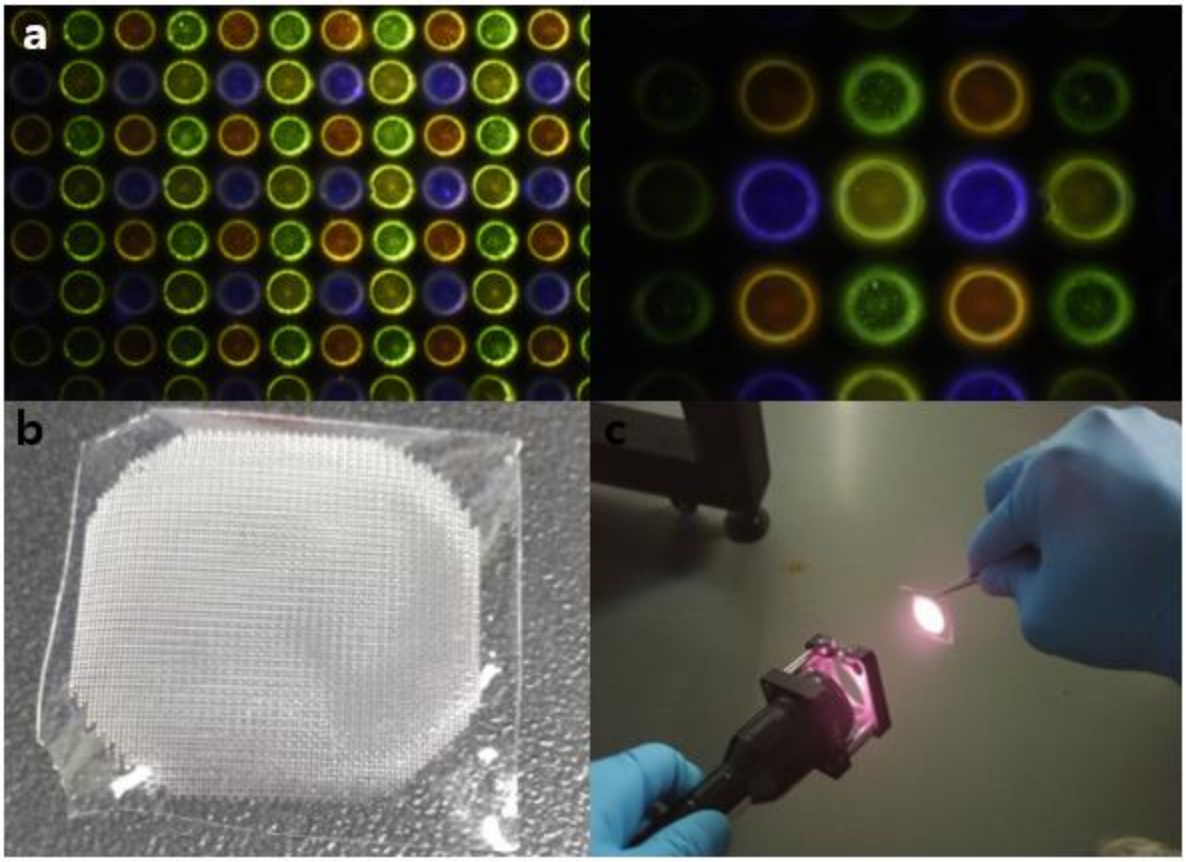


Figure 25. Multi-color microstructure array film. a) Optical image of 4 color microstructure array taken under 980 nm continuous-wave laser. Red array, blue array, green array, yellow array were made in order. Microstructure array was made of PEGDA with oxidized UCNs by contact lithography. (b) Microstructure which is made of PEGDA, was undamaged after detaching from glass. (c) Film which consists of microstructure array, absorbs 980nm IR and emits mixed visible light

4. Conclusion

We have demonstrated that microfabrication of photocurable resin can be realized by various methods. During fabrication, various types of production methods were discussed and tested. We have found that each method has a variety of advantages. To find optimal resin, various commercial photocurable resin such as HDDA, PUA, and PEGDA have been used and approved for use in each method. Furthermore, a new resin was synthesized and used to make the microstructure array. The use of highly useful photocurable resins in microstructure arrays can increase application possibilities. Furthermore, UCNs were introduced to apply this fabrication method in particular way. By adding UCNs, we could create a new concept of microstructure array that responds to near infrared rays. Because this is a type of microstructure array that is able to react immediately to near infrared rays, it is expected that it can be applied in various ways such as sensor or optical equipment.

5. Experimental section

5.1 UV-PDMS synthesis

4g of diglycidyl ether-terminated PDMS prepolymer(Mn 800g/mol), 39g of bis(hydroxyalkyl)-terminated PDMS prepolymer(Mn 5600g/mol) and 0.5g of N,N-diisopropylehtylamine were added in the round bottom flask. With vigorous stirring, the flask was heated to 110℃ for 60hours. Mixture of dichloromethane and aqueous 0.5N HCl was added to the flask to extract synthesized PDMS prepolymer. After separating the organic solvent layer, $MgSo_4$ was used to remove moisture and filtered. Solvent was evaporated under a reduced pressure using a vacuum pump and a viscous transparent silicon-based liquid (PDMS prepolymer with pendant hydroxyl group) was obtained. 2g of PDMS prepoylmer with pendant hydroxyl group was added in a small glass vial. 0.09g of 2-Isocyanatoethyl acrylate was added to the vial. 10mg of dibutyl tin dilaurate was then dropped into the vial. With vigorous stirring, the sample vial was left for 12h, then PDMS prepolymer with acrylate pendant group was obtained.

5.2 Flexible PUA synthesis

A mixture of 2 g isophorone diisocyanate (IPDI) and 0.1098 g dibutyltin dilaurate (DBTDL) in 10 mL of anhydrous THF was fed into a 100 mL flask. Nitrogen bubbling was carried out for 30 min to introduce inert environment. The mixture was heated to 50℃. A mixture of 7.1981 g Poly(tetrahydrofuran) (PTH)(Mn 2000 g/mol) in 35 mL anhydrous THF was added slowly in 1 h to reaction flask. The reaction was carried out for another 2.5 h at 50℃ with Nitrogen flow. A mixture of 0.8197 g 2-hydroxyethyl acrylate (HEA) and 0.1996 g 2-methyl-1 propanol in 5 mL anhydrous THF was added and the reaction was continued for another 1 h. Solution of 0.2668g of 2-methyl-1-propanol in 1 mL anhydrous THF was added and stirred another 30 mins to terminate polymerization reaction. Finally, anhydrous THF was evaporated by using a rotary evaporator and the liquid colorless resin was obtained after extraction with mixture diethyl ether and hexane at ratio 5:3 (v/v).

5.3 UCN synthesis

Below, mol % of RE^{3+} ion of final mixture for each color is described.

mol %	Red	Orange	Yellow	Green	Covalt	Skyblue	Blue	Purple	White
Gd^{3+}	30	30	30	30	30	30	30	30	30
Y^{3+}			38	50	49.7	51.775	51.8		38
Yb^{3+}	69.9	68	30	18	20	18	18	69.7	31.7
Er^{3+}	0.1	2	2	2	0.1	0.025		0.1	0.1
Tm^{3+}					0.2	0.2	0.2	0.2	0.2

4ml of 0.2M $RECl_3 \cdot 6H_2O$ aqueous solution (RE= Rare-earth metal (Gd, Y, Yb, Er, Tm)) was prepared. With vigorous stirring, 3ml of 0.2 g ml^{-1} NaOH aqueous solution, 10ml of ethanol, 10ml of oleic acid, 4ml of RECl3 solution and 2ml of 2M NH_4F aqueous solution were added into the chamber dropwise. After taking off the stirring bar, chamber was inserted into the autoclave. The autoclave was placed into the oven for 3 hours. After taking off the autoclave from the oven and it should be cool down overnight. After taking off the chamber from autoclave, product solution was centrifuged with ethanol and water.

5.4 UCN surface modification

5.4.1. UCN oxidation

Oxidation of UCNs was carried out as follows. 0.1 g of UCNs were added to a mixture of 100ml of cyclohexane, 70ml of tert-butanol, 10ml of water, and 5ml of 5 wt% K_2CO_3 solution and stirred at room temperature for about 20 minutes. Next, Lemieux-von Rudloff reagent was made by mixing 5.7Mm $KMnO_4$ and 0.1M $NaIO_4$ aqueous solution and then Lemiux-von Rudloff reagent was added dropwise to solution. The resulting mixture was stirred for 48 hours. The product was centrifuged and washed with deionized water, ethanol and acetone. After that, UCNs were dispersed in 50ml of hydrochloric acid (PH 4.0), and stirred for another 1 hour. The carboxy-terminated UCNs were washed 5 times with deionized water and collected by centrifugation

5.4.2 UCN silica coating

0.1 g of UCNs were added into 20ml of Triton X-100 solution. Solution was mixed by ultrasonication for 10 minutes form transparent solution, and then 80 mL of water was poured into the solution. The resulting mixture was stirred for 6 h. The product was centrifuged and washed with deionized water and the precipitation was dispersed in the mixture of 160ml of ethanol, 40ml of water and 2 mL of 28 wt% ammonia aqueous solution and then 0.06 g of TEOS was added. After stirring for another 6 h, the product was separated by centrifugation and then washed with ethanol and water.

5.5 microstructure array stage fabrication

5.5.1 PDMS Spin coating onto substrate

Mix 1.0 g PDMS curing agent (Sylgard 184) with 10.0 g PDMS base (Sylgard 184) for 30 s and allow the mixture to sit for 45 min to remove bubbles. Spincoate the PDMS mixture on 5cm X 5cm glass at 600rpm for 60s. Cure the PDMS spincoated glass in oven at 65℃ for 4 hours. Take off the PDMS coated glass from oven.

5.5.2 Spacer fabrication

Mix 1.0 g PDMS curing agent (Sylgard 184) with 10.0 g PDMS base (Sylgard 184) for 30 s and allow the mixture to sit for 45 min to remove bubbles. Spincoate the PDMS mixture on 5cm X 5cm glass at 600rpm for 60s. Cure the PDMS spincoated glass in oven at 65℃ for 4 hours. After taking off the PDMS coated glass from oven, cut off the PDMS and detach off the glass. Using oxygen plasma treatment, attach the spacer to PDMS coated glass. Oxygen plasma treatment is conducted at 100w for 60s.

5.5.3 Top glass fabrication

Mix 1.0 g PDMS curing agent (Sylgard 184) with 10.0 g PDMS base (Sylgard 184) for 30 s and allow the mixture to sit for 45 min to remove bubbles. Spincoate the PDMS mixture on 5cm X 5cm glass at 3000rpm for 100s. Cure the PDMS spincoated glass in oven at 65℃ for 4 hours. Take off the PDMS coated glass from oven.

5.5.4 Surface acrylation

Oxygen plasma treatment is conducted to the glass with the spacer at 100 W for 180s. Immerse the treated glass in 2% v/v 3-trimethoxysilylpropyl acrylate solution for 30 mins. After washing the glass, put it in oven at 65 65℃ for 1 hour. Take off the glass from oven.

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